Egg Shell
Onion Skin

THE SEPARATION OF GASES AND GASEOUS ISOTOPES BY MEANS OF THE ULTRACENTRIFUGE

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PREVIOUS WORK ON THE SEPARATION OF ISOTOPES OF GASES AND LIQUIDS BY CENTRIFUGING

In 1919 Lindemann and Aston (1) suggested centrifuging gases and liquids for the separation of their isotopes. For gases they showed the ratio of the quantities present at the center to the ratio of the quantities at the edge of the centrifuge rotor would be K_o where

$$K = e^{-\frac{v^2}{2RT}(M_1 - M_2)}$$

and where v = linear speed of the periphery

R = universal gas constant

T = absolute temperature

M_1 = molecular weight of heavier isotope

M_2 = molecular weight of lighter isotope

for a gas containing two isotopes. Assuming a maximum peripheral speed of 1.3×10^5 cm/sec and difference of molecular weights of 2, at ordinary temperatures a single operation would give fractions with a change of K of 0.65.

Lindemann and Aston further pointed out that for liquids, such as lead, it is difficult to form an accurate idea of the quantities without a knowledge of the equation of state. If compression is neglected and the lead treated as a solution in the other, a similar equation holds.

In 1920 Joly and Poole (2) attempted to separate the isotopes of lead by means of the centrifuge. No evidence of any separation was obtained. Poole (3) presented a paper in 1921 giving the derivation of

(1) Lindemann and Aston, Phil. Mag. 37, 523, 1919.
(2) Joly and Poole, Phil. Mag. 39, 372, 1920.
(3) Poole, Phil. Mag. 41, 818, 1921.

$$\chi = \sigma_{\infty} \frac{EK\Sigma}{A_S} (\delta^{\infty} - \delta^{0})$$

an equation for the separation of isotopes in liquid form which is essentially the same as given by Lindemann and Aston. From this he showed that the separation to be expected in his experiment with Joly corresponded to a change in density of only one part in 30,000 which would have been very difficult to detect.

In 1922 Mulliken (4,5) reviewed the possibility of separating isotopes by centrifuging and also suggested a method in which gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate slowly, the light fractions being drawn off slowly at low pressure from the center of the rotor. Mulliken made an unsuccessful attempt to separate the isotopes of mercury by centrifuging.

Beams and Pickels (6) in 1935 described an air driven turbine capable of producing very high rotational speeds and suitable for driving rotors suitable for centrifuging gases or liquids.

Beams and Haynes (7) first reported in 1936 a successful separation of a mixture of two gases of different molecular weight by means of a centrifuge driven by a Beams-Weed turbine or top. later in 1936 Beams and Haynes (8) reported a separation of some of the isotopes of chlorine by the method of evaporative centrifuging. The two latter references are reports on the work described in some detail in this paper.

(4) Mulliken, Jour. Amer. Chem. Soc. 44, 1033, 1922.
(5) Mulliken, Jour. Amer. Chem. Soc. 45, 1592, 1923.
(6) Beams and Pickels, R.S.I. 6, 299, 1935.
(7) Beams and Haynes, Phy. Rev. 49, 64, 1936.
(8) Beams and Haynes, Phys. Rev. 1936.

(1) Bowers and Sedgwick, Inc., 1972.

(2) Hamilton, John, Chairman, Subcommittee on Water Resources, Committee on Public Works, U.S. House of Representatives, 1971.

(3) Hamilton, John, Chairman, Subcommittee on Water Resources, Committee on Public Works, U.S. House of Representatives, 1972.

THE SEPARATION OF NITROGEN AND CARBON DIOXIDE BY MEANS OF THE CENTRIFUGE

Theory

If a mixture of two gases of different molecular weights are placed in a rotor and whirled, a partial separation would be expected due to centrifuge action. To oppose this action there is diffusion caused by thermal agitation. The separation to be expected after equilibrium is reached can be readily calculated. Consider a round rotor, Fig. 1, with a radial hole of A cm^2 cross section, the axis of rotation being perpendicular to the paper. Let there be a mass of gas m of small volume located r cm from the center of the rotor. Then the centrifugal force on the gas will be

$F = \frac{mv^2}{r}$ v being the linear speed of m.

Now $m = \rho dV = \rho A dr$

where ρ is the density of the gas and dV the volume of the gas.

Thus $F = \frac{\rho A v^2 dr}{r}$

The resulting outward pressure of the gas is

$$d = \frac{F}{A} = \frac{\rho v^2 dr}{r} \qquad (1)$$

In the gas law, assuming the ideal gas,

$PV = RT$

Where V is the volume of 1 mol of gas and R the universal gas constant.

Then since $V = \frac{M}{\rho}$

$\frac{PM}{\rho} = RT$

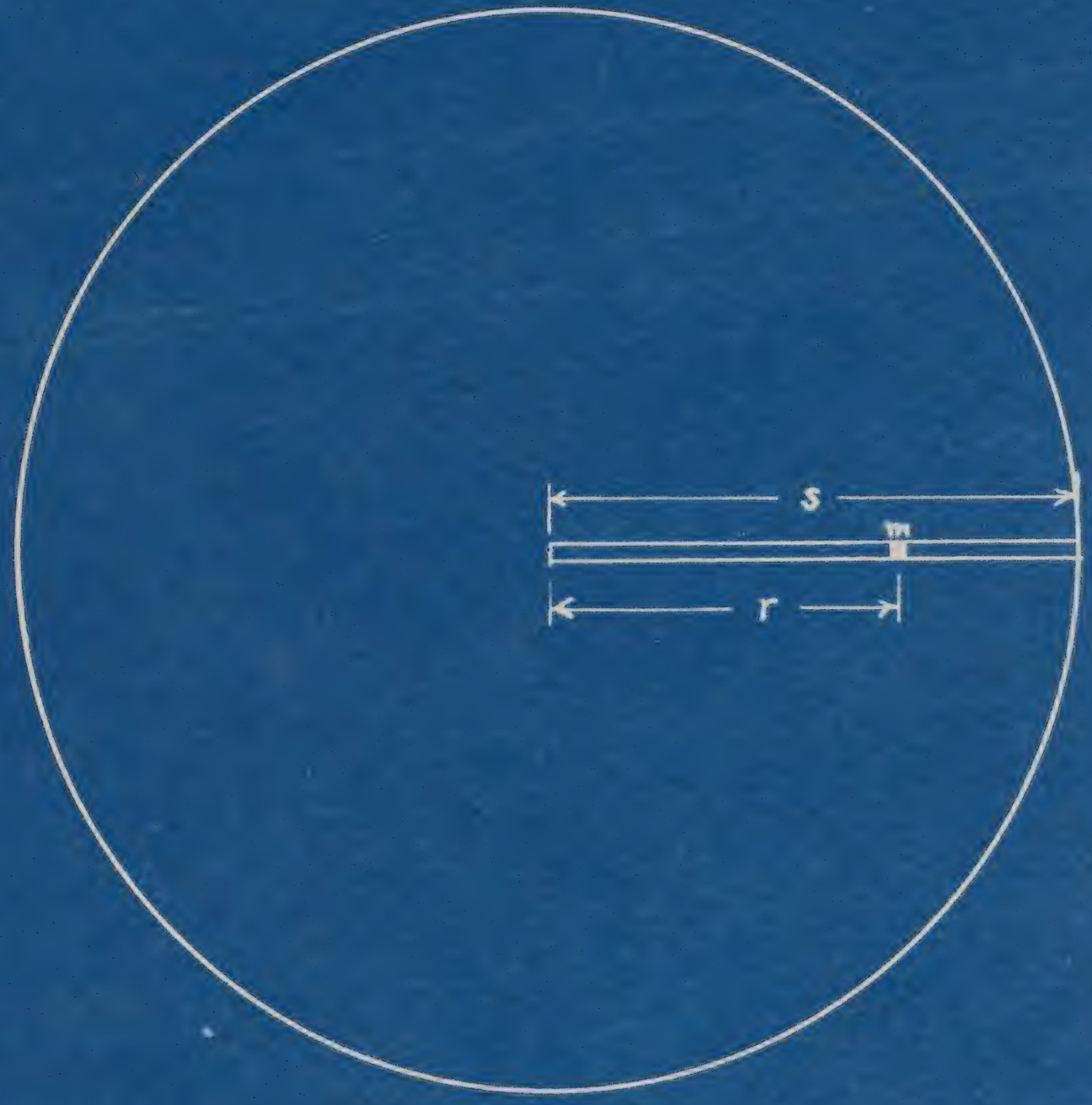


Fig. 1

or

$$P = \frac{RT\rho}{M}$$

and $dP = \frac{RT}{M} d\rho$ if T is kept constant.

Combining with (1)

$$\frac{RT}{M} d\rho = \rho \frac{v^2}{r} dr$$

or $$\frac{d\rho}{\rho} = \frac{M}{RT} \frac{v^2}{r} dr = \frac{M}{RT} w^2 r dr$$

where w is the angular velocity

Integrating

$$\left[\log \rho\right]_{\rho_o}^{\rho} = \left[\frac{M}{RT} \frac{w^2 r^2}{2}\right]_0^s$$

where ρ_o is the density of the gas at the center, ρ the density at the periphery and s the radius of the rotor.

This gives

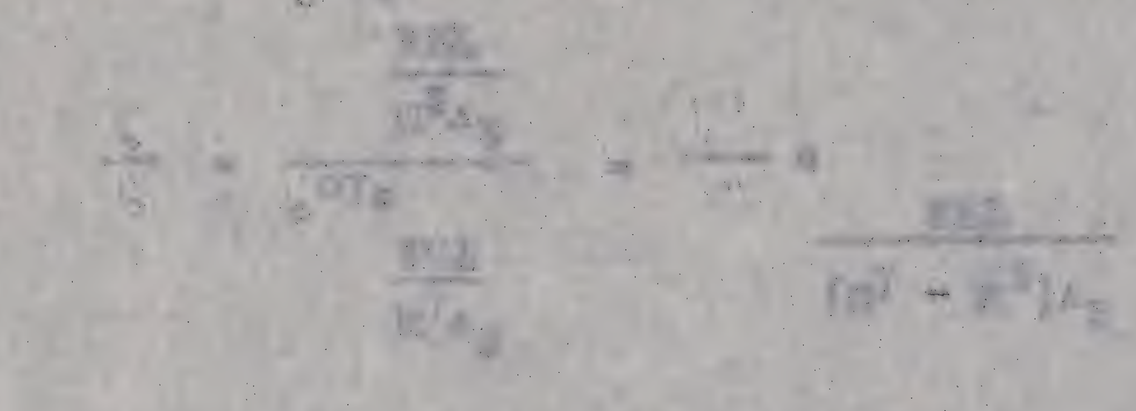
$$\rho = \rho_o e^{\frac{Mw^2 s^2}{2RT}} = \rho_o e^{\frac{Mv^2}{2RT}}$$

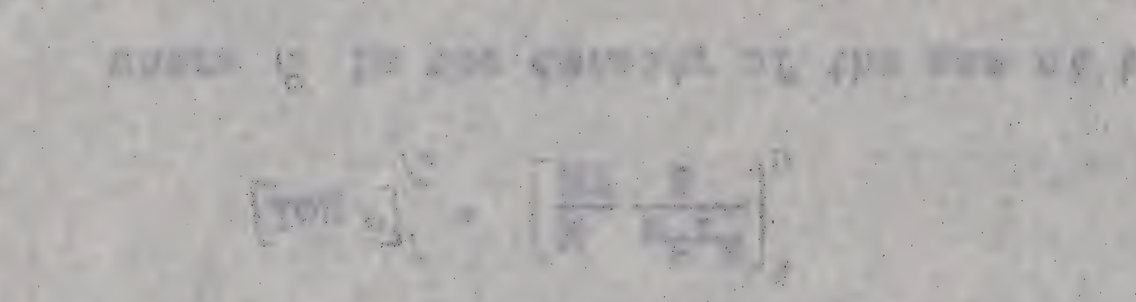
which shows how the density of a single gas at the periphery varies with velocity, temperature, and molecular weight.

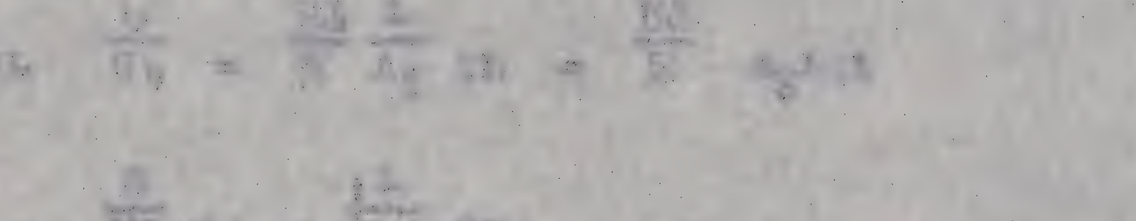
If two gases of different molecular weights are present, from Dalton's law the ratio of their concentrations at the periphery in terms of their concentrations at the center will then be

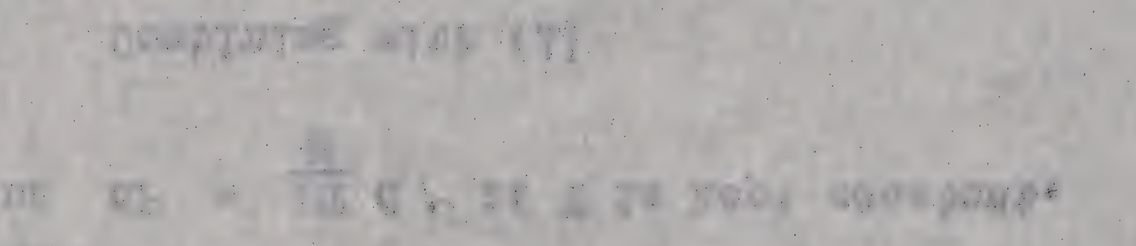
$$\frac{\rho_1}{\rho_2} = \frac{\rho_{o1} e^{\frac{M_1 v^2}{2RT}}}{\rho_{o2} e^{\frac{M_2 v^2}{2RT}}} = \frac{\rho_{o1}}{\rho_{o2}} e^{\frac{(M_1 - M_2)v^2}{2RT}}$$

where ρ_{o1} is the density of the first gas at the center and ρ_{o2} the density of the second gas at the center. Sometimes it is desirable to express









the ratio of the concentrations of the two gases at the center of the rotor in terms of their concentrations at the periphery, in which case,

$$\frac{\rho_{o1}}{\rho_{o2}} = \frac{\rho_1}{\rho_2} e^{-\frac{(M_1 - M_2)v^2}{2RT}} \quad \text{or} \quad \frac{\rho_1}{\rho_2} e^{\frac{(M_2 - M_1)v^2}{2RT}}$$

If the ratio of the mass concentrations of gas 1 and gas 2 at the center of the rotor be called K_o and the ratio of the concentrations of gas 1 and gas 2 at the periphery be called K then

$$\frac{K_o}{K} = e^{\frac{(M_2 - M_1)v^2}{2RT}}$$

this ratio being called the separation factor of one gas with respect to the other.

Applying this to the specific case of the separation of nitrogen and carbon dioxide one has

$$S_{N_2} = \frac{K_o}{K} = \frac{\frac{\rho_{oN_2}}{\rho_{oCO_2}}}{\frac{\rho_{N_2}}{\rho_{CO_2}}} = e^{\frac{(M_{CO_2} - M_{N_2})v^2}{2RT}} = e^{\frac{(44.00 - 28.02)v^2}{2 \times 8.316 \times 10^7 \times 300}}$$

$$= e^{3.21 \times 10^{-10} v^2}$$

for a temperature of 300 A, where S_{N_2} is called the separation factor for nitrogen and v the linear speed at the periphery of the rotor. This relation between S_{N_2} and v is shown graphically in Fig. 2.

The ratio of the fractional concentration of nitrogen with respect to carbon dioxide at the periphery to the fractional concentration at the center of the rotor would, of course, be the reciprocal of S_{N_2} given above. This relation is shown graphically in Fig. 3.

Separation factor, centrifuge action, for N_2 referred to CO_2 in terms of velocity (theoretical) $T = 300^{\circ}$ A.

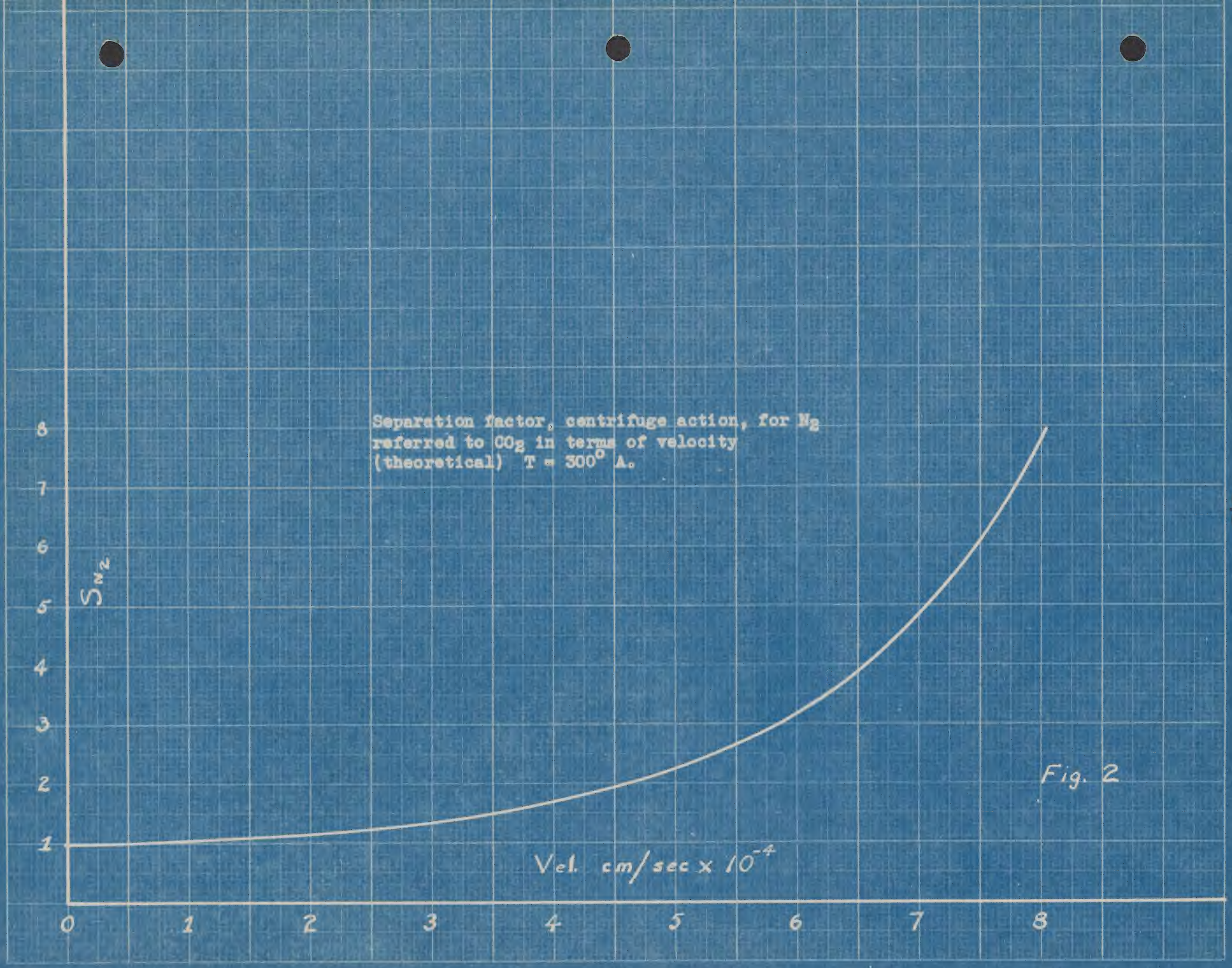
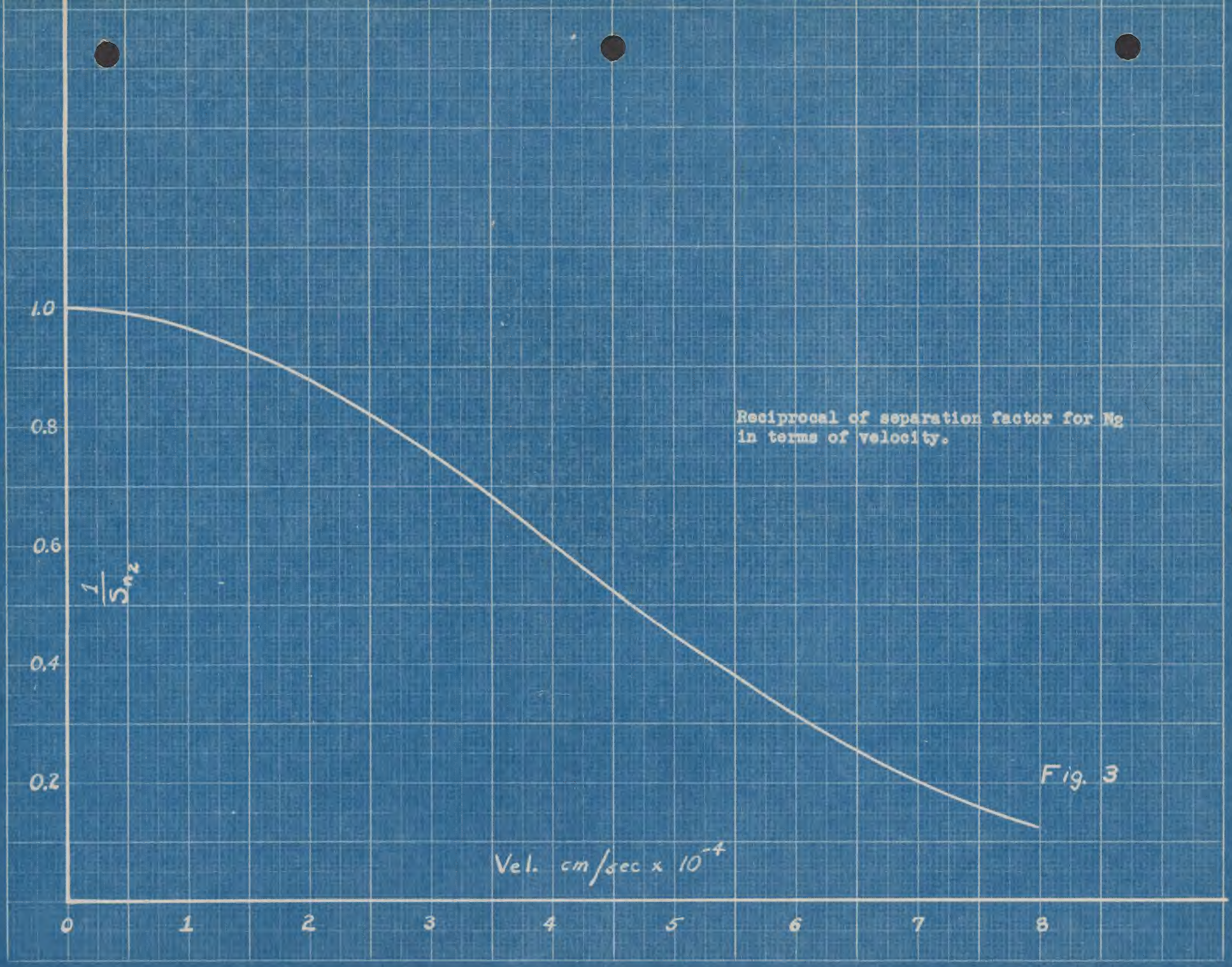


Fig. 2



Reciprocal of separation factor for Mg in terms of velocity.

Fig. 3

It would seem that in some cases the use of this reciprocal separation factor would have certain advantages over the use of the more commonly used separation factor. For example, it is to be noted that, over the range of velocities used, the relation between $\frac{1}{S_{N_2}}$ and velocity is more nearly linear than between S_{N_2} and velocity. It is also to be noted that the possible range of $\frac{1}{S_{N_2}}$ is from unity to zero while the possible range of S_{N_2} is from unity to infinity. For purposes of plotting the use of $\frac{1}{S_{N_2}}$ would be more convenient than S_{N_2}, particularly where the range of v is large.

It is of interest in experimental work, in this connection, to note the effect of error in determining the percentage change in gas concentrations on the S_{N_2} - v curve and the $\frac{1}{S_{N_2}}$ - v curve for various values of velocity. These errors are augmented graphically in the S_{N_2} - v curve for large values of v but are augmented graphically in the $\frac{1}{S_{N_2}}$ - v curve for small values of v. This is shown clearly in Fig. 4, the vertical thickness of the curves showing the possible limits of variation for S_{N_2} and $\frac{1}{S_{N_2}}$ respectively, for a uniform $\pm$ 1% error in the determination of the concentrations of nitrogen and carbon dioxide where these gases are bing separated. It is assumed that the initial concentrations before separation are equal.

Curves showing possible effect of error of ± 1% in the determination of concentrations of nitrogen and carbon dioxide on S_N and its reciprocal for various velocities.

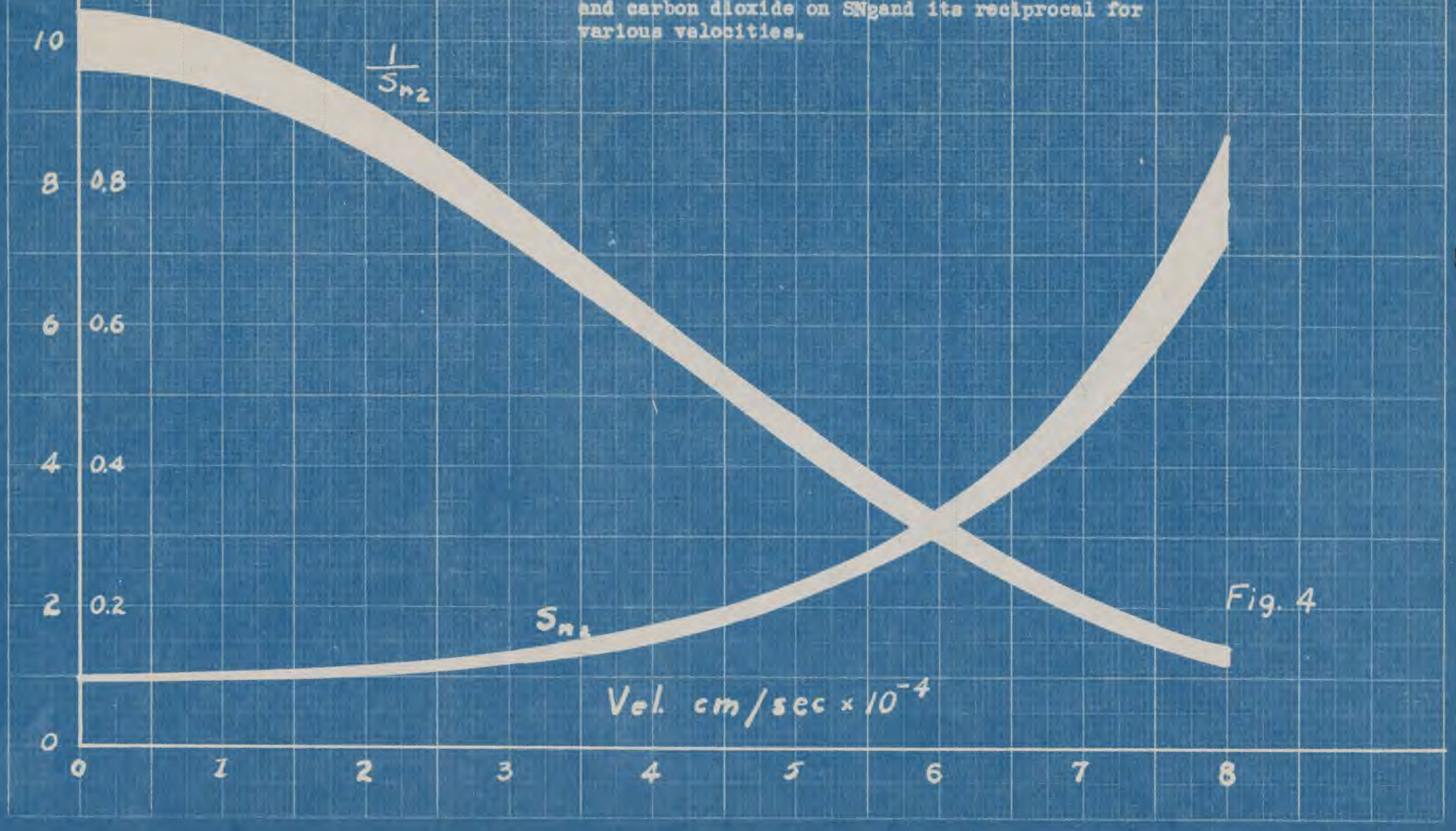


Fig. 4

EXPERIMENT (ROUND ROTOR)

Apparatus

The apparatus used for experimentally testing the theory of the separation of two gases of slightly different density by means of the centrifuge is shown schematically in Figure 5. It consists essentially of four parts as follows: (1) The gas supply which supplies the necessary mixture of, in this case, carbon dioxide and nitrogen at a constant pressure, and at the desired rate; (2) the centrifuge itself; (3) the vacuum system, including the necessary pumps, gauges and drying tubes; and (4) the gas analysis apparatus for determining the percentage of carbon dioxide both for the initial mixture and the mixture after having been run through the centrifuge.

(1) The Gas Supply. The constant pressure gas tank is shown in the lower lefthand corner of Figure 5. The gas mixture is held in G over S.A.E. 10 cylinder oil. Weight W serves to nearly counterbalance the weight of the inverted cylinder. R is a rubber hose connection which was taken loose when the gas mixture was inserted at G and then replaced when the apparatus was in use. The reversed jet at J, which consists of a capillary tube drawn down, serves to admit the gaseous mixture to the centrifuge at the proper rate. The stopcock S, serves to cut off the gas supply.

(2) The Centrifuge. The centrifuge C, shown in Figure 5 only schematically is very similar in general design to that described by Beams and Pickels (9). A cross section showing some detail of one of

(9) Beams and Pickels, Review of Scientific Instruments, 6, 305, 1935.

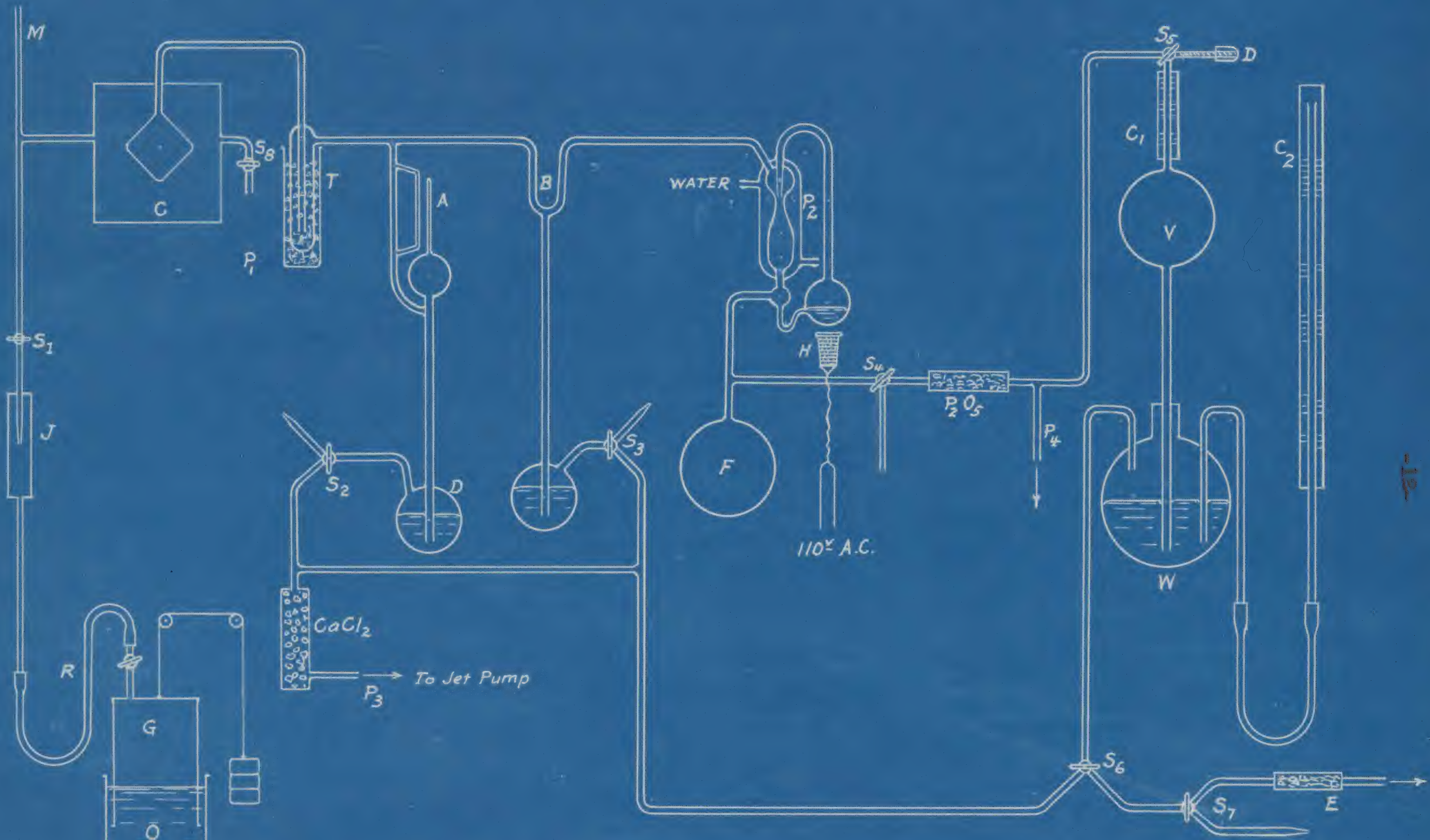

M
S8
C
T
P1
A
B
WATER
P2
S5
D
C1
C2
V
S1
J
S2
D
S3
F
H
S4
P2O5
P4
110v A.C.
W
CaCl2
To Jet Pump
P3
R
G
O
S6
S7
E

Fig. 5

the later designs used is shown in Figure 6. After the air was removed from the chamber C by means of the vacuum pumps, the gaseous mixture CO_2 and N_2 was admitted through the opening A. A lighter mixture of the gas was pumped through the tube D and out through the opening at E, the residual gas through opening at B.

R is the rotor which has radial holes extending from the periphery to the center connecting with the tube D by means of a special packing gland at the top of the rotor (not shown). Tube D, which is stainless steel, serves the two-fold purpose of a shaft for the rotor and passage way for the lighter mixture of gases to the upper chamber from which the gas is pumped through the opening E. Opening F serves as an oil overflow line from the upper half of the upper bearing. This opening is connected to a glass flask of some 500 ml capacity.

G_1 and G_2 are bearings. These bearings are double in that each has two actual bearing surfaces, as shown, one at the top of the bearing assembly and one at the bottom. Both bronze and babbit were used for these with some success. The bearing assemblies are fully supported by rubber rings, H. The bearing assembly is hollow, oil being forced into them through the channels shown, from the oil tank I. This oil tank is circular and goes completely around the top. Compressed air at about 15 lb/in^2 is led into the oil tank through J.

The shaft D is driven by means of an air turbine K. The jets are placed around the turbine, compressed air being supplied through opening M into chamber L.

The air bearing taking care of the vertical thrust due to the weight of the rotor and assembly, is one of the most important features of the centrifuge.[1] Compressed air from I passes to a chamber immediately below the turbine K. Air then passes out between a bakelite collar N

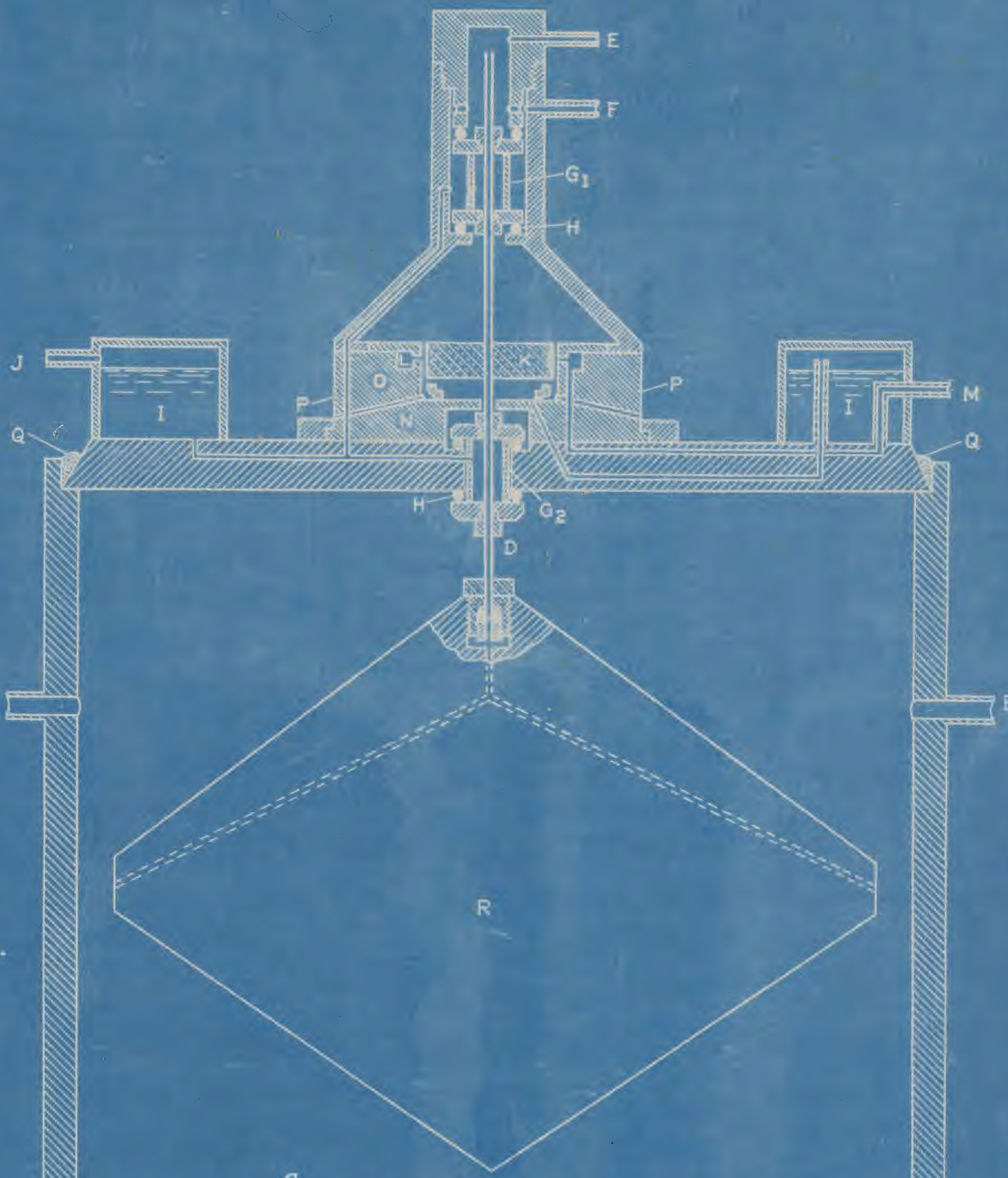


Fig. 6

and the turbine K, forming a thin film of air at O which supports the rotor assembly.

P, P serves as exhaust ports for the turbine. The vacuum chamber is sealed from the atmosphere by using Apiegon sealing compound "Q" at Q.

The speed of the rotor and turbine is determined by stroboscopic means. A spot of black paint is placed on the upper surface of the turbine. This is viewed by a system of mirrors through a series of holes placed in a disk near its periphery, the disk being mounted on the horizontal shaft of a variable speed motor. If the turbine makes one revolution while the line of sight passes from one hole in the disk to the next hole, the turbine appears to remain stationary. Then, if the speed of the disk is known, which can be determined with the aid of a revolution counter and stopwatch, and the number of holes in the disk known, the speed of the turbine and rotor can be readily calculated.

As an example, let us suppose the speed of the motor is adjusted until the spot on the turbine appears stationary. If there are no holes in the disk and the motor makes 120 revolutions in one minute, the speed of the turbine is 120 x 60 = 7200 revolutions per minute.

Since the turbine will also appear to remain stationary if two, three, four, etc. holes pass the line of sight for each revolution of the rotor and also if the turbine turns two, three, four, etc. revolutions for one hole passing the line of sight, care must be exercised in making the observations.

The spot appears most distinct when one hole passes the line of sight for one revolution of the turbine. Even so, it is best to have some method of checking the approximate speed. In this experiment the

speed was checked by using the beat note method. This consisted of operating a 1000 cycle tuning fork, humming into a loud speaker and observing the beat note made between this and the musical note produced by the centrifuge whose frequency in cycle per second corresponded to the speed of rotation in revolution per second. A little practice made this an easy matter.

With a little experience it was even possible to estimate approximately the speed of rotation from this musical note by ear without the aid of the electric tuning fork.

The rotors used were made of Dow Metal and Duralumin, both of which have a high ratio of tensile strength to density. They were shaped in such a way as to be relatively strong.

(3) The Vacuum System. A mechanical pump is connected to P_1 (Fig. 5) to remove gas residue from the chamber C. T is a cold trap in which a mixture of solid carbon dioxide and alcohol were used. This trap served to prevent mercury vapor from passing back into the centrifuge.

A is a McLeod gauge used for measuring the pressure at that point in the system. The mercury is raised in the gauge by admitting air at atmospheric pressure through stopcock S_2. The mercury is again lowered in the gauge by turning stopcock S_2 so as to remove the air above the mercury at D. This is done by the jet pump connected to the calcium-chloride drying tube at P_3. B is a mercury cut-off. Mercury is admitted to the cut-off by admitting air at atmospheric pressure through stopcock S_3.

The mercury vapor diffusion pump is shown at P_2. This is heated electrically. The liter bulb F serves as a reservoir between the

diffusion pump and the fore-pump connected at P_4. The drying tube shown next to the pump connection P serves to keep water vapor from the gas-analysis apparatus described below.

The right-hand part of the T connection at P_4 connects to the gas-analysis apparatus.

(4) The Gas Analysis Apparatus. This consists essentially of an arrangement for compressing a given volume of gas to a known pressure, and volume, absorbing the carbon dioxide, and finally redetermining the pressure and corresponding volume. Such a process allows a determination of the carbon dioxide content of the gas from the centrifuge.

S_5 is a three-way stopcock. D is the absorption tube which contains a mixture of ascarite and soda-lime. V has a volume of about 1 liter and connects below to a flask W which contains some liter and a half of mercury. C_1 and C_2 are scales used for determining volumes and pressures of the gas.

To operate, air is admitted at atmospheric pressure through stopcocks S_6 and S_7 to W. This forces mercury into the flask V and up to the stopcock S_5, the absorption tube D being shut off. After allowing the apparatus to stand several minutes a sample of the gas is drawn into V by connecting W to the jet pump through S_6. When V is filled with gas, S_5 is turned so that the supply and D are both shut off. The gas in V is then compressed, by proper manipulation of S_6 and S_7, into the glass tube immediately above V. In so doing the pressure is raised until it is easily obtained by taking readings of the mercury columns at C1 and C2. The volume is obtained from the cross section of the tube C1 and reading of the mercury column there.

This compressed gas is now forced into the ascarite tube D which has been previously treated to remove all occluded air. The gas is washed back and forth into and out of D until all the carbon dioxide is absorbed. The mercury is then removed from V reducing the pressure in D to the same or slightly lower pressure as it had in the beginning. D is again shut off and the gas recompressed. During this operation it is essential that S_5 be turned so as not to admit new gas.

The new pressure and volume of the compressed gas is then observed and the percentage of carbon dioxide calculated.

It is assumed that the volume of D is negligible as compared with V.

It is to be noted that S_7 is connected through E to a 20 lb/in^2 air source, which is often needed to compress the gas sufficiently.

This apparatus differs from the usual form of carbon-dioxide analysis apparatus in that the determinations are made in terms of volume rather than weight; hence the apparatus can be used to analyze volumes of gas of the order of 1 cm^3 (STP) or less without the use of delicate chemical balances.

Procedure

After the centrifuge and system were completely assembled the pumps P_2 and P_4 were operated for some two or three hours with S_1 and S_3 closed. If no leaks were present the McLeod gauge showed a pressure of 5 microns or less corresponding roughly to the vapor pressure of the oil used in the centrifuge.

A mixture of carbon dioxide and air, of about 50% each, was placed in the container G. The stopcocks S_1 and S_3 were then opened allowing the gaseous mixture to pass slowly through the jet at J_1 into the centrifuge chamber C and out through the pump P_1 and, at the same time, out through the vacuum system T, A, B, etc. After allowing the system to come to a condition of equilibrium, a measurement was made of the carbon dioxide content of the gas mixture, the centrifuge not running.

The centrifuge was then brought up to the speed desired, and, after maintaining this speed for several minutes, a sample of the gas passing through the round rotor of the centrifuge was taken and analyzed. When possible, more than one sample was analyzed at a given speed of the rotor. Observations were obtained for several speeds of the rotor.

Due to difficulties encountered at the high rotational speeds, such as breakage, etc., observations were made with different rotors with slightly different diameters. This does not affect the results, however, as this fact is taken into proper consideration.

Observations and Results

Observations and results are given below for the separation of carbon dioxide and nitrogen by means of the centrifuge, using the round rotor with radial holes, for various speeds of the centrifuge.

The horizontal lines or breaks in the table indicate a change in the initial gas mixture and perhaps also a change in the diameter of the rotor.

It is to be noted that the horizontal rows go in pairs, the first giving the readings for pressure and volume before the carbon dioxide is absorbed (P_1 and V_1) and the second the readings for pressure and volume after the gas is passed into the absorption tube (P_2 and V_2).

Glossary of Symbols Used in the Table

D is the diameter of the rotor.

W is the angular velocity of the rotor.

V is the linear speed of the periphery of the rotor.

L is the reading of the mercury column on scale C_1 of the gas analysis apparatus, and is the length of the gas column at that point. Please refer to Fig. 5. This reading is directly proportional to the volume of the gas at that point since the diameter of the tube is uniform.

R is the reading of the mercury column on scale C_2 of the gas analysis apparatus.

$R_{cor.}$ is the corrected reading of R so as to make the reading of the C_2 scale refer to the same zero as the C_1 scale. The scales of C_1 and C_2 did not have the same zero.

B is the barometer reading.

P is the pressure on the confined gas.

F is the ratio $\frac{P_2V_2}{P_1V_1}$ x 100 which is the % by volume of nitrogen of the gas mixture.

S_{N_2} is the separation factor referred to nitrogen which the ratio of the fraction % nitrogen and % carbon dioxide by volume or weight after separation to the fraction % nitrogen and % before separation.

$$\text{Thus} \qquad S_{N_2} = \frac{\frac{N_2^1}{CO_2^1}}{\frac{N_2}{CO_2}}$$

Equivalence of S_{N_2} for Mass Concentrations, Molecular Concentrations and Volume Concentrations

$$S_{N_2} = \frac{\frac{\rho' N_2}{\rho' CO_2}}{\frac{\rho N_2}{\rho CO_2}}$$

Take any volume of gas, say $v = 1\ cm^3$

Then, $N_2 = \frac{m' N_2}{v}$, $CO_2 = \frac{m' CO_2}{v}$ etc.

and $$S_{N_2} = \frac{\frac{m' N_2}{m CO_2}}{\frac{m N_2}{m CO_2}}$$

The mass of any gas

$m = N\mu$

where N = number of molecules per cm^3 if m = mass per cm^3.

and μ = mass of 1 molecule

Here $m_{N_2} = N_{N_2}$ x mass of 1 molecule of N_2, etc.

$$S_{N_2} = \frac{\frac{N'_{N_2} \times \mu_{N_2}}{N'_{CO_2} \times \mu_{CO_2}}}{\frac{N_{N_2} \times \mu_{N_2}}{N_{CO_2} \times \mu_{CO_2}}} = \frac{\frac{N'_{N_2}}{N'_{CO_2}}}{\frac{N_{N_2}}{N_{CO_2}}}$$

which is the value of S_{N_2} in terms of molecular concentrations.

This obviously may be written by simple manipulation

$$\frac{\frac{N'_{N_2} KT}{N'_{N_2} KT + N'_{CO_2} KT} \times 100}{\frac{N'_{CO_2} KT}{N_2 'KT + N'_{CO_2} KT} \times 100} = \frac{\frac{N'_{N_2} KT}{N'_{N_2} KT + N'_{CO_2} KT} \times 100}{\frac{(N'_{N_2} - N'_{N_2} + N_{CO_2})KT}{N'_{N_2} KT + N'_{CO_2} KT} \times 100}$$

the same for unprimed values — same for unprimed values

$$= \frac{\frac{N'_{N_2} KT}{N'_{N_2} KT \quad N'_{CO_2} KT} \times 100}{\frac{100 - \frac{N'_{N_2} KT}{N'_{N_2} KT + N'_{CO_2} KT} \times 100}{\text{same for unprimed values}}}$$

where K and T may be taken for the Boltmann constant and absolute temperature respectively.

Now $PV = NKT$

$$\text{Hence} \quad S_{N_2} = \frac{\frac{\rho'_{N_2} V'_{N_2}}{(\rho'_{N_2} + \rho'_{CO_2}) V_{mix}} \times 100}{100 - \frac{\rho'_{N_2} V'_{N_2}}{(\rho'_{N_2} \quad \rho'_{CO_2}) V_{mix}} \times 100}$$

same for unprimed values

and by Dalton's law of partial pressure

$$= \frac{\frac{\rho'_{N_2} V'_{N_2}}{\rho'_{mix} V'_{mix}} \times 100}{100 - \frac{\rho'_{N_2} V'_{N_2}}{\rho'_{mix} V'_{mix}} \times 100}$$

same for unprimed values

or in terms of notation used later simply

$$= \frac{\frac{P_2'V_2'}{P_1'V_1'} \times 100}{100 - \frac{P_2'V_2'}{P_1'V_1'} \times 100}$$

same for unprimed values

which is the value of S_{N_2} in terms of volume concentrations

Since $\frac{P_2V_2}{P_1V_1} \times 100$ or $\frac{P_2'V_2'}{P_1'V_1'} \times 100$ is the per cent by volume of N_2 and $100 - \frac{2V_2}{1V_1} \times 100$ is the per cent by volume of CO_2, this may also be written

$$S_{N_2} = \frac{\frac{\% N_2'}{\% CO_2'}}{\frac{\% N_2}{\% CO_2}} \quad \text{or simply} \quad \frac{\frac{N_2'}{CO_2'}}{\frac{N_2}{CO_2}}$$

D	W	v	L - V	R	R cor.	B	P	F	S
cm	rev/sec	cm/sec	cm	cm	cm	cm Hg	cm Hg		
10.0	0	0	20.0	81.1	51.1	75.17	44.1		
			12.3	82.3	52.3		35.2	49.1	
	0	0	21.0	85.9	55.9		40.3		
			13.2	86.5	56.5		31.9	48.3	
	1000	3.14×10^4	10.3	94.5	64.5		21.0		
			7.1	94.6	64.6		17.7	58.3	1.47
	1090	3.42 "	8.7	95.0	65.0		18.9		
			6.0	94.7	64.7		16.5	60.1	1.57
	1200	3.77 "	6.5	97.5	67.5		14.2		
			5.1	98.3	68.3		12.0	66.3	1.92
10.0	0	0	19.7	81.9	51.9	75.08	42.9		
			12.3	81.8	51.8		35.6	51.8	
	0	0	18.9	81.2	51.2		42.8		
			11.8	81.1	51.1		35.8	52.3	
	1480	4.65 "	10.6	96.5	66.5		19.2		
			8.2	97.1	67.1		16.2	65.3	1.71
	1520	4.78 "	9.4	95.9	65.9		18.6		
			7.1	95.6	65.6		16.6	67.4	1.91
9.75	0	0	13.0	90.6	60.6		27.2		
			8.8	90.8	60.8		22.8	56.8	
	0	0	12.2	91.0	61.0		26.0		
			8.3	91.0	61.0		22.1	57.7	
	1720	5.27 "	8.0	98.5	68.5		14.3		
			7.1	98.6	68.6		13.3	82.5	3.55
	1910	5.85 "	7.6	98.3	68.3		14.1		
			6.6	97.4	67.4		14.0	86.5	4.7
	2000	6.12 "	7.9	97.9	67.9		14.8		
			7.4	98.0	68.0		14.2	90.0	6.8

Centrifuge chamber pressure varied from 1 to 2 millimeters of mercury

A Sample Calculation of S_{N_2}

In order to illustrate the method used in obtaining the separation factor S_{N_2} for various speeds, a specific case will be taken and followed, step by step.

Suppose we find the value of S_{N_2} for W = 1000 rev/sec from the above data. It will be necessary, first, to find the per cent of nitrogen in the initial mixture of carbon dioxide and nitrogen before being run through the centrifuge. The absolute pressure (P) on the confined gas is obviously the barometric pressure less the difference in height of the two mercury columns, or, $P = B - (R_{cor.} - L)$. For the first horizontal line in the table this gives P = 75.2 - (51.1 - 20.0) = 44.1 cm Hg (the scales read down). This value, it is to be remembered, is the pressure on the confined gas mixture <u>before</u> the carbon dioxide is absorbed. The second horizontal row of figures in the table contains readings of L and R for the remaining nitrogen after the carbon dioxide is removed by absorption. By a similar process the pressure is then found to be P = 75.2 - (52.3 - 12.3) = 35.2 cm Hg.

Calling the first pressure and volume P_1 and V_1 respectively and the second pressure and volume P_2 and V_2 the per cent of nitrogen (+ oxygen) in the mixture is given by $\frac{P_2V_2}{P_1V_1} \times 100 = \frac{433}{882} \times 100 = 49.1$

As a check on this determination a second set of observations were made on a new sample of gas. This gave the percentage of nitrogen as 48.3. The average value 48.7% was used in computations.

With the centrifuge running at 1000 revolutions per second a value of 58.3% was obtained.

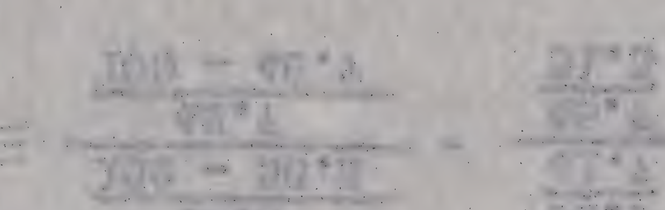
The separation factor (for nitrogen) is the ratio of the fraction of nitrogen over the fraction of carbon dioxide after passing through

the centrifuge to the fraction of nitrogen over the fraction of carbon dioxide before passing through the centrifuge.

Or $S_{N_2} \equiv \frac{\frac{N_2'}{CO_2'}}{\frac{N_2}{CO_2}}$, where the prime symbols refer to the respective fractions after separation. See discussion on equivalence of S_{N_2} for mass and volume concentration given above.

In this case S_{N_2} is

$$S_{N_2} \equiv \frac{\frac{58.3}{100 - 58.3}}{\frac{48.7}{100 - 48.7}} = \frac{\frac{58.3}{41.7}}{\frac{48.7}{51.3}} = 1.47$$



Value of % N_2 Final in Terms of Separation Factor and % N_2 Initial

It is sometimes desirable to pass directly back from the separation factor to % N_2 final (% N_2), that is, to find the new % of N_2 for a given separation factor. This can be accomplished readily as follows:

By definition $$S_{N_2} = \frac{\frac{N_2'}{CO_2'}}{\frac{N_2}{CO_2}}$$

Then $$S_{N_2} = \frac{N_2'}{CO_2'} \times \frac{CO_2}{N_2} = \frac{\% N_2' \ (100 - \% N_2)}{(100 - \% N_2') \% N_2}$$

For simplicity let

$$S = S_{N_2}$$

$$a = \% N_2'$$

$$b = \% N_2$$

Then $$S = \frac{100a - ab}{100b - ab}$$

$$100bS - abS = 100a - ab$$

$$a = \frac{100bS}{100 - b + bS}$$

or $$\% N_2' = \frac{100 \times \% N_2 \times S_{N_2}}{\% N_2 \ (S_{N_2} - 1) + 100}$$

Results

The separation factor obtained for various speeds is shown graphically in Fig. 7. The crosses show the experimental values with the solid line approximating an average. For comparison the dotted line shows the theoretical values, the same as shown in Fig. 2. It is to be noted that the experimental values of separation factor run somewhat higher than the theoretical values, particularly for higher speeds.

Test for Leaks

The usual precautions and tests were made to keep leaks in the system to a minimum. For added assurance a special test was made immediately after obtaining the highest values of S_{N_2} corresponding to the highest speeds. The system was allowed to stand closed with no pumps running for a period of 18 hours. The pressure change as shown by the manometer M was 1.2 cm Hg. The system was pumped down again and the pumps cut off. Stopcock S_1 was then opened as for normal running. The time required for the pressure to again reach 1.2 cm was less than 8 minutes. The ratio of times for the same pressure change was $\frac{8}{1080}$ or less than 0.8 of 1%. Assuming a uniform pressure change this would indicate roughly an error of less than 0.8 of 1% for leaks. As a matter of fact, there is good reason to believe a large part of the pressure change during the 18-hour stand was due to vapor from the oil.

An additional test was made at this time with the centrifuge running but with the pumps off and S_1 closed. The run was for 37 minutes. No pressure in the centrifuge chamber could be observed.

Solid curve is for experimental values of S_{N_2}
Dotted curve gives theoretical values.

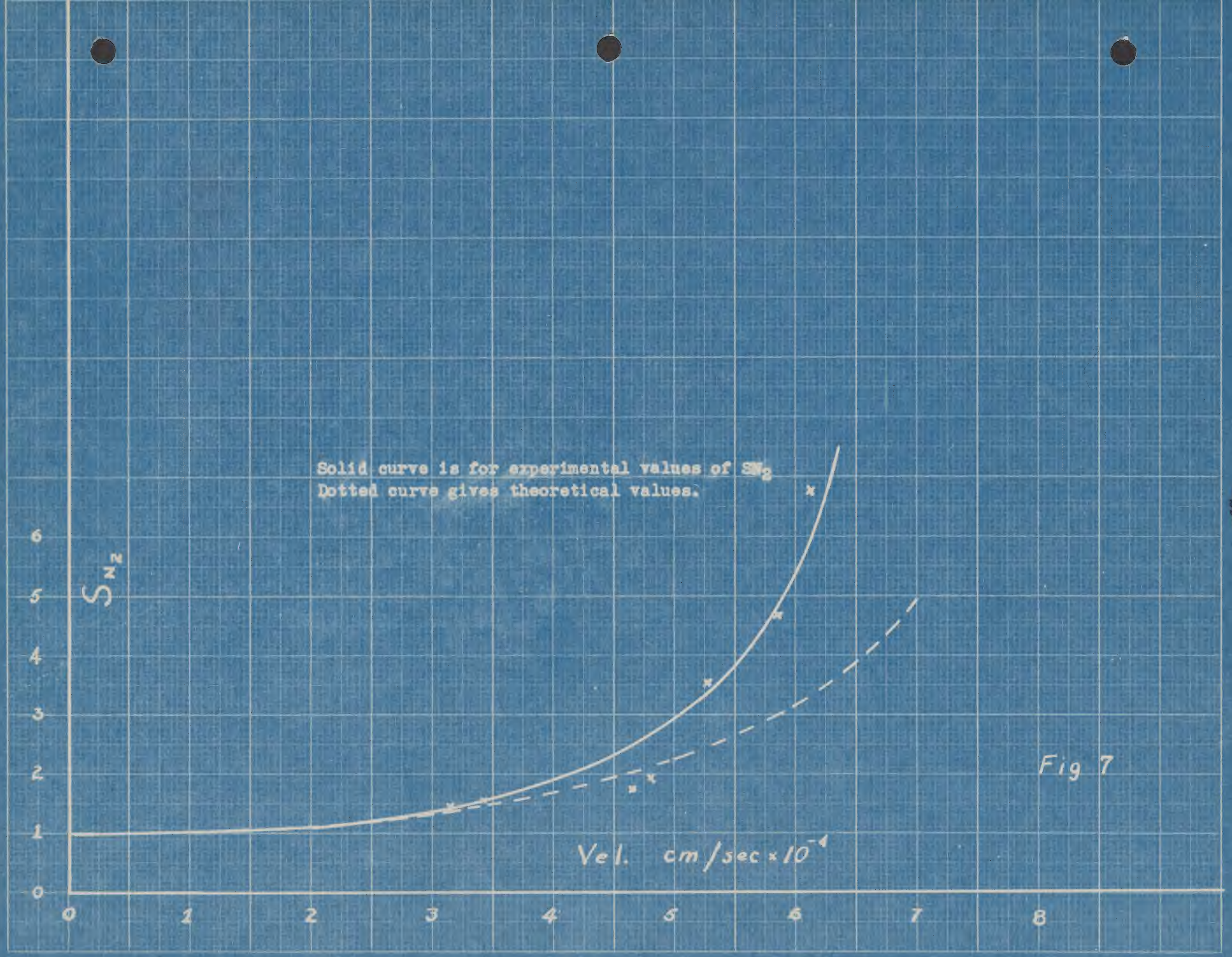


Fig 7

The Separation of Nitrogen and Carbon Dioxide by Means of the Centrifuge Using the Principle of Velocity Selection

If the rotor of the centrifuge is made as shown in the horizontal section, Fig. 8, and rotated about an axis perpendicular to the paper, in the direction indicated by the arrow, only those molecules having a speed greater than that of the openings would be able to enter the rotor. In a mixture of two gases having different molecular weights, kinetic theory shows that the heavier molecules will have a lower mean speed. Such a rotor, then, placed in a mixture of two such gases and rotated at a speed that would give the openings in the rotor a linear speed comparable with that of the mean speed of the gas molecules, would give rise to a partial separation of the two gases. The separation would be in such a direction as to aid the separation caused by centrifuge action, the percentage of the lighter gas being greater at the center of the rotor than at the periphery.

The amount of separation for a given pair of gases can be calculated from the kinetic theory. Since the molecules of a given gas at a given temperature do not all have the same velocity but have a certain velocity distribution, the first step is to determine what this velocity distribution will be.*

Let c = velocity of any molecule.

Let x, y and z = coordinates.

Let u, v, and w = components of c along the axes x, y, and z.

Then $c^2 = u^2 + v^2 + w^2$

* The following derivation of the Maxwellian distribution of velocities is taken from Loeb "The Kinetic Theory of Gases."

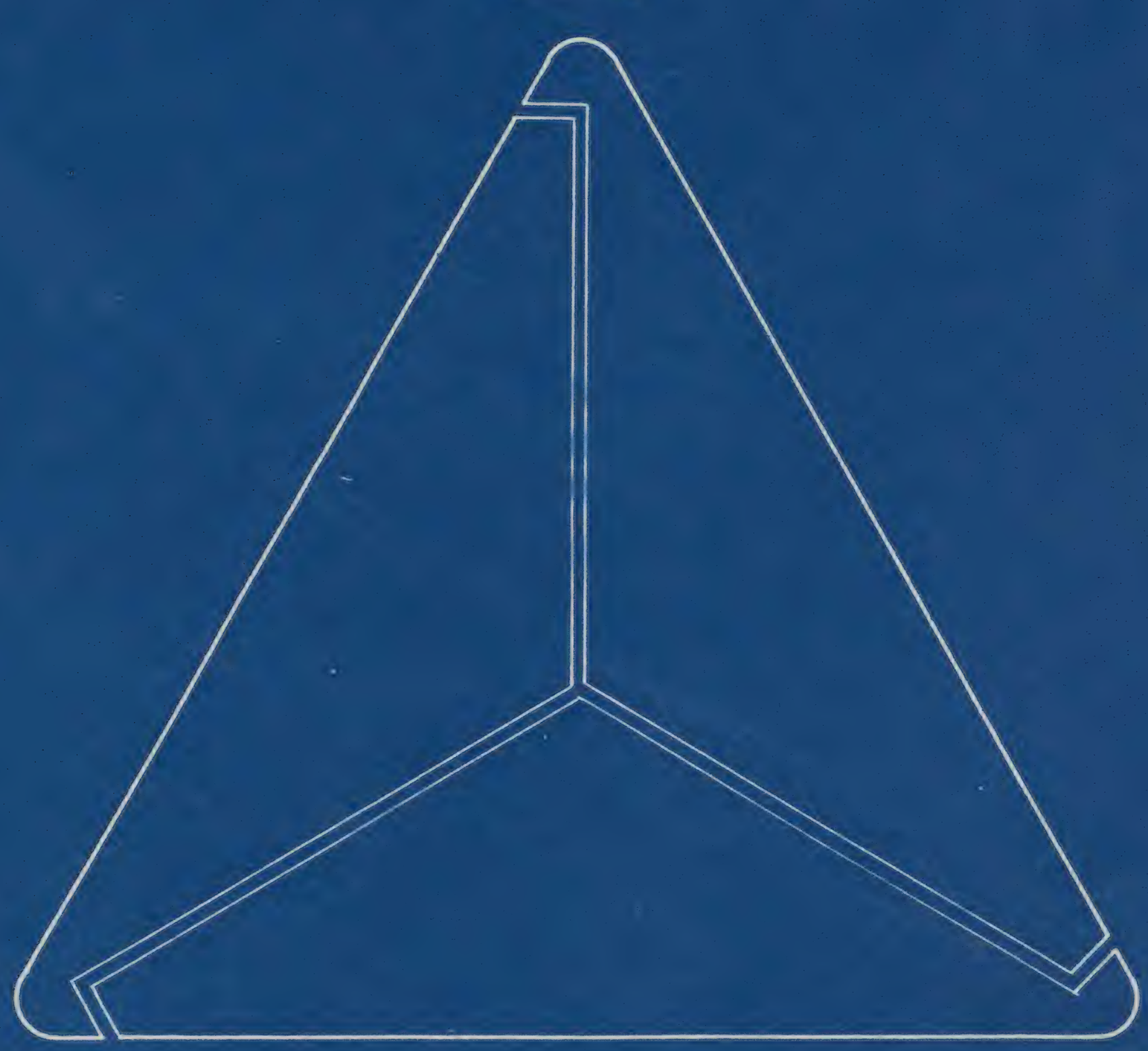


Fig. 8'

Let us assume that the chance that a velocity component lies between u and u + du is a function of u only which may be written f(u)du. Similarly the probability of a velocity component lying between v and v + dv is f(v)dv and between w and w + dw is f(w)dw.

Let us assume further that the velocities along any three coordinate axes are independent of each other. Then we may write that the probability of a velocity vector lying simultaneously between u and u + du, v and v + dv, and w and w + dw is

$$f(u)f(v)f(w)\,du\,dv\,dw.$$

The chance that the single vector c ends in the volume element du dv dw may similarly be written

$$F(c)\,du\,dv\,dw$$

or for convenience

$$\phi(c^2)\,du\,dv\,dw$$

If it is immaterial what coordinate system the results are expressed in, we may write

$$f(u)f(v)f(w)\,du\,dv\,dw = \phi(c^2)\,du\,dv\,dw$$

or

$$f(u)f(v)f(w) = \phi(u^2 + v^2 + w^2)$$

For a particular value of c, $\phi(c^2)$ is constant.

Then

$$f'(u)f(v)f(w)\,du + f(u)f'(v)f(w)\,dv + f(u)f(v)f'(w)\,dw = 0$$

and $$\frac{f'(u)}{f(u)}\,du + \frac{f'(v)}{f(v)}\,dv + \frac{f'(w)}{f(w)}\,dw = 0$$

Also since $c^2 = u^2 + v^2 + w^2$

$$u\,du + v\,dv + w\,dw = 0$$

or $$\lambda u\,du + \lambda v\,dv + \lambda w\,dw = 0 \quad \text{where } \lambda = \text{const.}$$

Adding to the above

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right)du + \left(\frac{f'(v)}{f(v)} + \lambda v\right)dv + \left(\frac{f'(w)}{f(w)} + \lambda w\right)dw = 0$$

Since the velocity components are independent of each other each term must be zero.

$$\frac{f'(u)}{f(u)}\,du = -\lambda u\,du$$

$$\frac{f'(v)}{f(v)}\,dv = -\lambda v\,dv$$

$$\frac{f'(w)}{f(w)}\,dw = -\lambda w\,dw$$

$$\log f(u) = -\frac{\lambda}{2}u^2 + \log A$$

$$\log f(v) = -\frac{\lambda}{2}v^2 + \log A$$

$$\log f(w) = -\frac{\lambda}{2}w^2 + \log A$$

$$f(u) = A\,e^{-\frac{\lambda}{2}u^2}$$

$$f(v) = A\,e^{-\frac{\lambda}{2}v^2}$$

$$f(w) = A\,e^{-\frac{\lambda}{2}w^2}$$

Writing

$$\frac{\lambda}{2} = \frac{1}{\alpha^2}$$

$$f(u)\,du = A\,e^{-\frac{u^2}{\alpha^2}}\,du$$

$$f(v)\,dv = A\,e^{-\frac{v^2}{\alpha^2}}\,dv$$

$$f(w)\,dw = A\,e^{-\frac{w^2}{\alpha^2}}\,dw$$

If there are N molecules per cm^3, the number having a velocity u, v, and w are respectively

$$N_{du} = N A e^{-\frac{u^2}{\alpha^2}} du$$

$$N_{dv} = N A e^{-\frac{v^2}{\alpha^2}} dv$$

$$N_{dw} = N A e^{-\frac{w^2}{\alpha^2}} dw$$

Evaluation of A and α

$$N = \int_{-\infty}^{+\infty} N_u = \int_{-\infty}^{+\infty} N A e^{-\frac{u^2}{\alpha^2}} du = N A \int_{-\infty}^{+\infty} e^{-\frac{u^2}{\alpha^2}} du$$

Then $$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$N = N A \sqrt{\frac{\pi}{\frac{1}{\alpha^2}}} = N A \alpha \sqrt{\pi}$$

$$A = \frac{1}{\alpha \sqrt{\pi}}$$

and $$N_{du} = \frac{N}{\alpha \sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du$$

Similarly, $$N_{dv} = \frac{N}{\alpha \sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}} du$$

$$\text{and} \qquad N_{dw} = \frac{N}{\alpha\sqrt{\pi}} e^{-\frac{w^2}{\alpha^2}} dw$$

$$\text{Also} \qquad f(u)du = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du$$

$$f(v)dv = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}} dv$$

$$f(w)dw = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{w^2}{\alpha^2}} dw$$

From above we write that the probibility that a velocity vector lies between u and u + du, v and v + dv, and w and w + dw is

$$f(u)f(v)f(w)du\ dv\ dw = \frac{1}{\alpha^3\ \pi^{\frac{3}{2}}} e^{-\frac{(u^2+v^2+w^2)}{\alpha^2}} du\ dv\ dw$$

$$\text{or} \quad f(u)f(v)f(w) = \frac{1}{\alpha^3\ \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}}$$

The chance that this velocity vector ends between c and c + dc is

f(u)f(v)f(w) x volume contained in sperical shell c and c + dc

$$\text{or} \quad \frac{1}{\alpha^3\ \pi^{\frac{3}{2}}} e^{-\frac{c^2}{\alpha^2}} \times 4\pi c^2 dc = \frac{4c^2}{\alpha^3\ \pi^{\frac{1}{2}}} e^{-\frac{c^2}{\alpha^2}} dc$$

For N molecules the number ending in the volume c to c + dc is

$$N_{dc} = \frac{4Nc^2}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} dc$$

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This function is 0 for $c = 0$ and also 0 for $c = \infty$ and has only positive values in between. The maximum for this function corresponds to the most probable speed. The value of this most probable speed is found by differentiating and equating to 0.

$$\frac{dN_{dc}}{dc} = \frac{4N}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} \cdot 2c\,dc - \frac{4Nc^2}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} \cdot \frac{2c}{\alpha^2}\,dc = 0$$

or $c = \alpha$,

or α is the most probable speed.

For convenience in plotting, the equation for N_{dc} may also be written in the form

$$N_{dc} = \frac{4N}{\sqrt{\pi}} \frac{c^2}{2} e^{-\frac{c^2}{\alpha^2}} \frac{dc}{\alpha}$$

The curve in Fig. 8 shows graphically the relation between N_{dc} and $\frac{c}{\alpha}$ for $\frac{dc}{\alpha} = 0.1$

and $N = 1000$

Value of α in Terms of R

According to the gas law

$$p\,v = R_1 T$$

Now p equals the change in momentum per sec by wall of a container 1 cm on an edge divided by its area of 1 cm^2.

Maxwellian velocity distribution

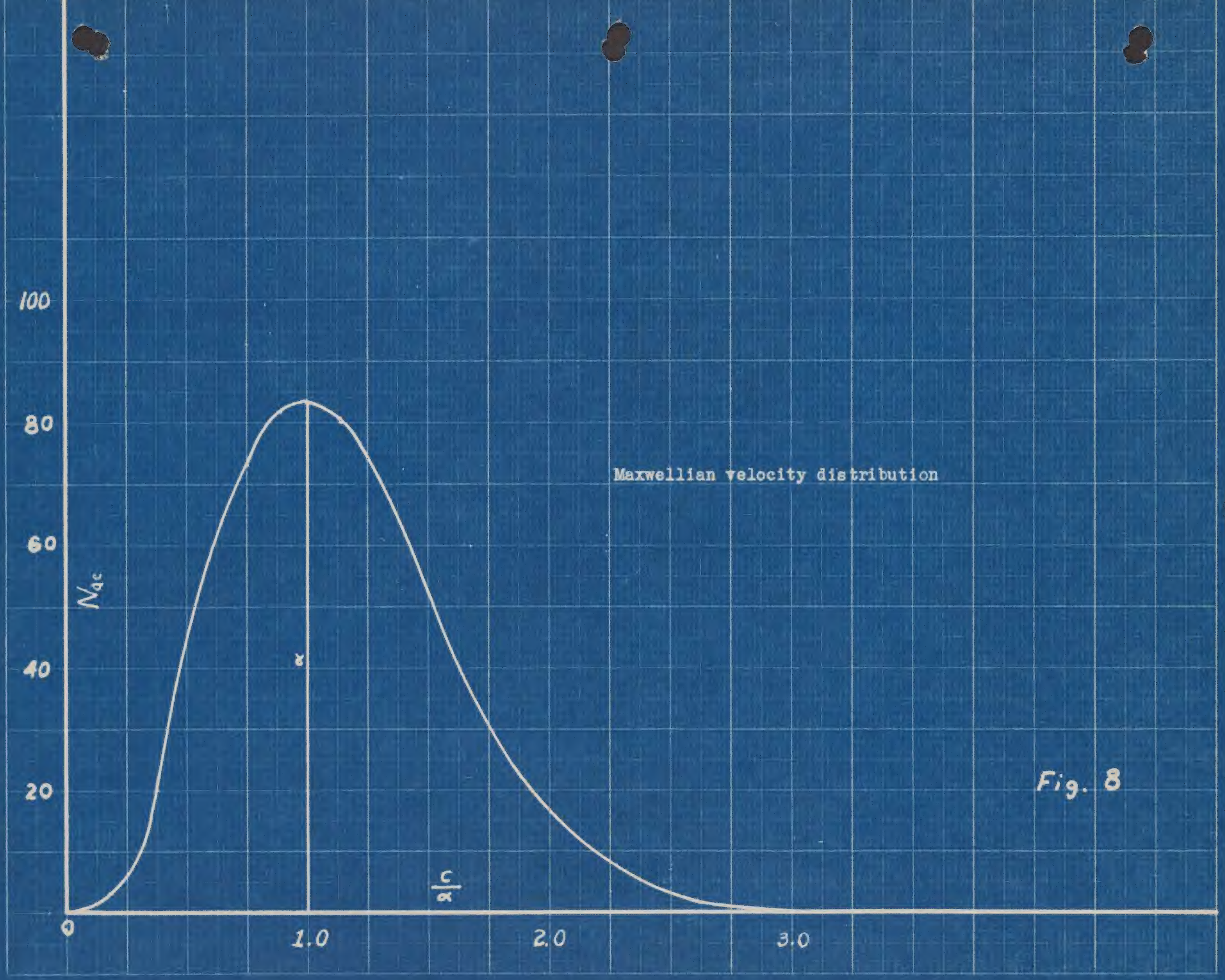


Fig. 8

$$p = 2m \frac{C \times NC}{2} \times \frac{1}{3}$$

where 2mC is the change of momentum of one molecule, $\frac{NC}{2} \times \frac{1}{3}$ is the number of hits on one face of the cube per sec.

where m = mass of 1 molecule

C = root mean square velocity

N = number of molecules per cm^3

Then $p = \frac{1}{3} NmC^2$

and $pv = \frac{1}{3} NmC^2 = R_1T$

but $C = \sqrt{\frac{3}{2}}\alpha$ *

then $\frac{Nm\alpha^2}{2} = R_1T$

N_m is the mass of 1 cm^3 of gas and R_1 refers to 1 cm^3 of gas.

If R is expressed in terms of 1 gram-mol the equation becomes

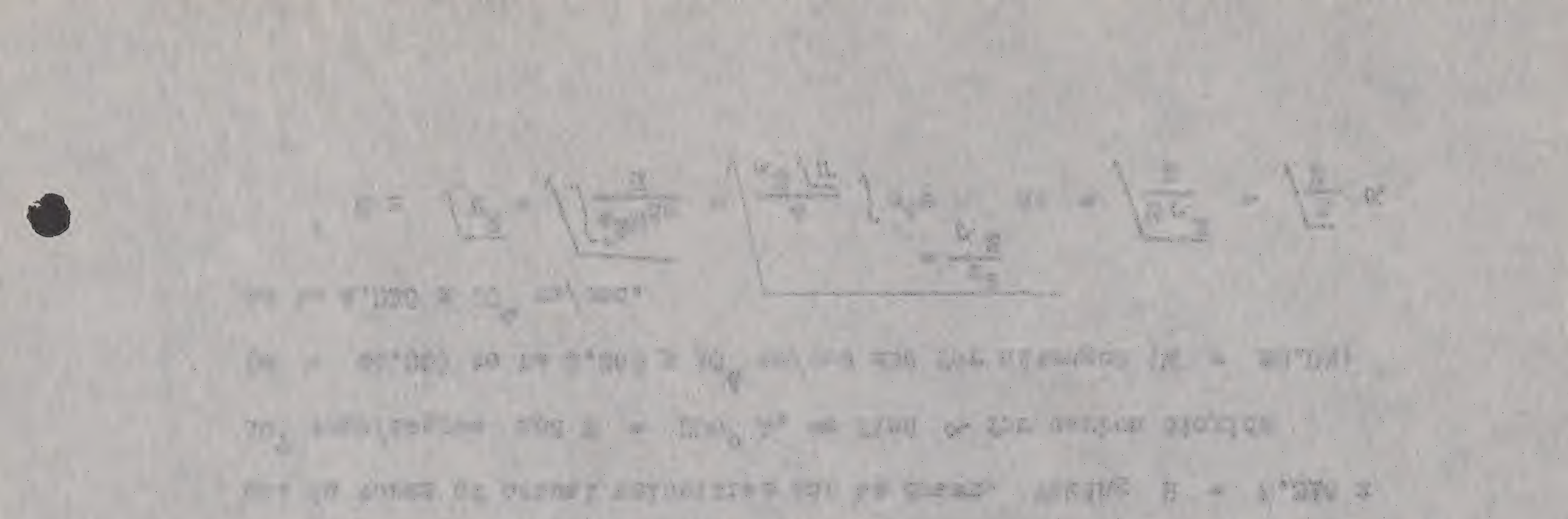
$$\frac{M\alpha^2}{2} = RT$$

or $$\alpha^2 = \frac{2RT}{M}$$

or $$\alpha = \sqrt{\frac{2RT}{M}}$$

Now that the value of α has been determined in terms of the gram-molecular weight of the gas, the velocity distribution curve for a given gas in terms of actual velocities can be drawn. Taking R = 8.316 x 10^7 ergs/degree and T = 300° A, we find α for carbon dioxide (M = 44.00) to be 3.368 x 10^4 cm/sec and for nitrogen (M = 28.02) to be 4.220 x 10^4 cm/sec.

* $C \equiv \sqrt{\overline{c^2}} = \sqrt{\int_0^\infty \frac{c^2 N dc}{N}} = \sqrt{\frac{4}{\alpha^3\sqrt{\pi}} \int c^4 e^{-\frac{c^2}{\alpha^2}} dc} = \sqrt{\frac{3\alpha^2}{2}} = \sqrt{\frac{3}{2}}\alpha$



Using the relation

$$N_{dc} = \frac{4Nc^2}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} dc$$

and taking dc = 1.1 x 10^4 cm/sec and N = 10,000, one obtains the velocity distribution curves for CO_2 and N_2 shown in Fig. 9. It is to be noted that the most probable velocities correspond to the above values for α.

Number of Molecules Entering the Rotor

In order to simplify the problem let us assume for the time being that for a given periphal speed of the rotor all of the molecules having a speed greater than this particular value will enter the rotor. In order to calculate the number of molecules entering the rotor, therefore, it will be necessary to sum up all of the molecules having speeds between that of the holes in the rotor and infinity.

Thus $$\int_c^\infty dN = N_c^\infty = \int_c^\infty \frac{4Nc^2}{\sqrt{\pi}\,\alpha^3} e^{-\frac{c^2}{\alpha^2}} \frac{dc}{\alpha}$$

where N_c^∞ is the number desired.

For convenience we may consider the fraction of molecules having velocities above a certain value rather than the actual number. Thus

$$\int_c^\infty \frac{dN}{N} = \int_x^\infty \frac{4}{\sqrt{\pi}} \frac{c^2}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} \frac{dc}{\alpha}$$

Let $x = \frac{c}{\alpha}$

Then $$\int_c^\infty \frac{dN}{N} = \int_x^\infty \frac{4}{\sqrt{\pi}} x^2 e^{-x^2} dx$$ where the lower limit x

Maxwellian velocity distribution for CO_2 and N_2

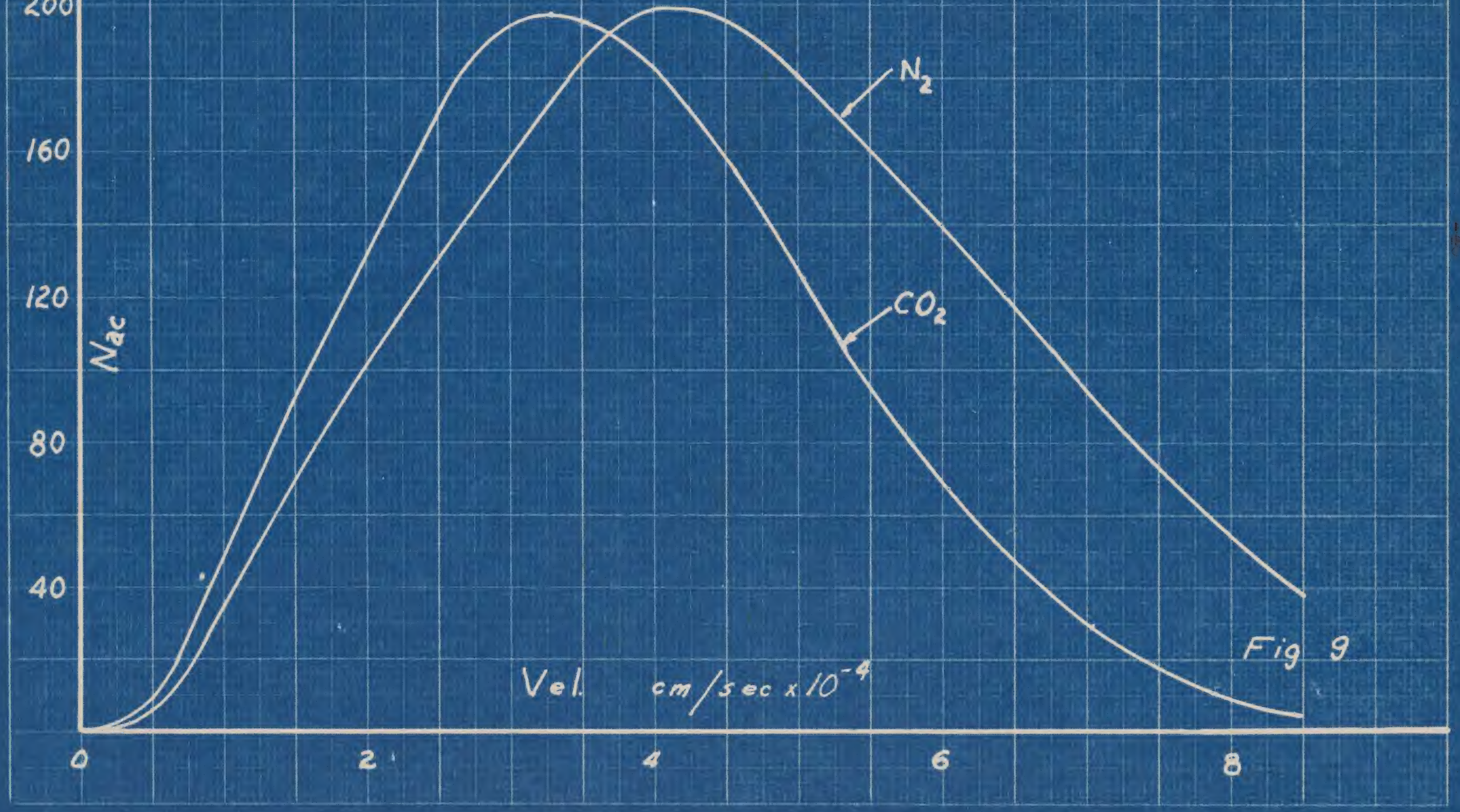


Fig 9

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corresponds to a lower limit $c = \alpha x$

Integrating by parts, letting

$$v = e^{-x^2}$$

$$dv = -2xe^{-x^2}\,dx$$

$$u = -x$$

where $\int udv = uv - \int vdu$

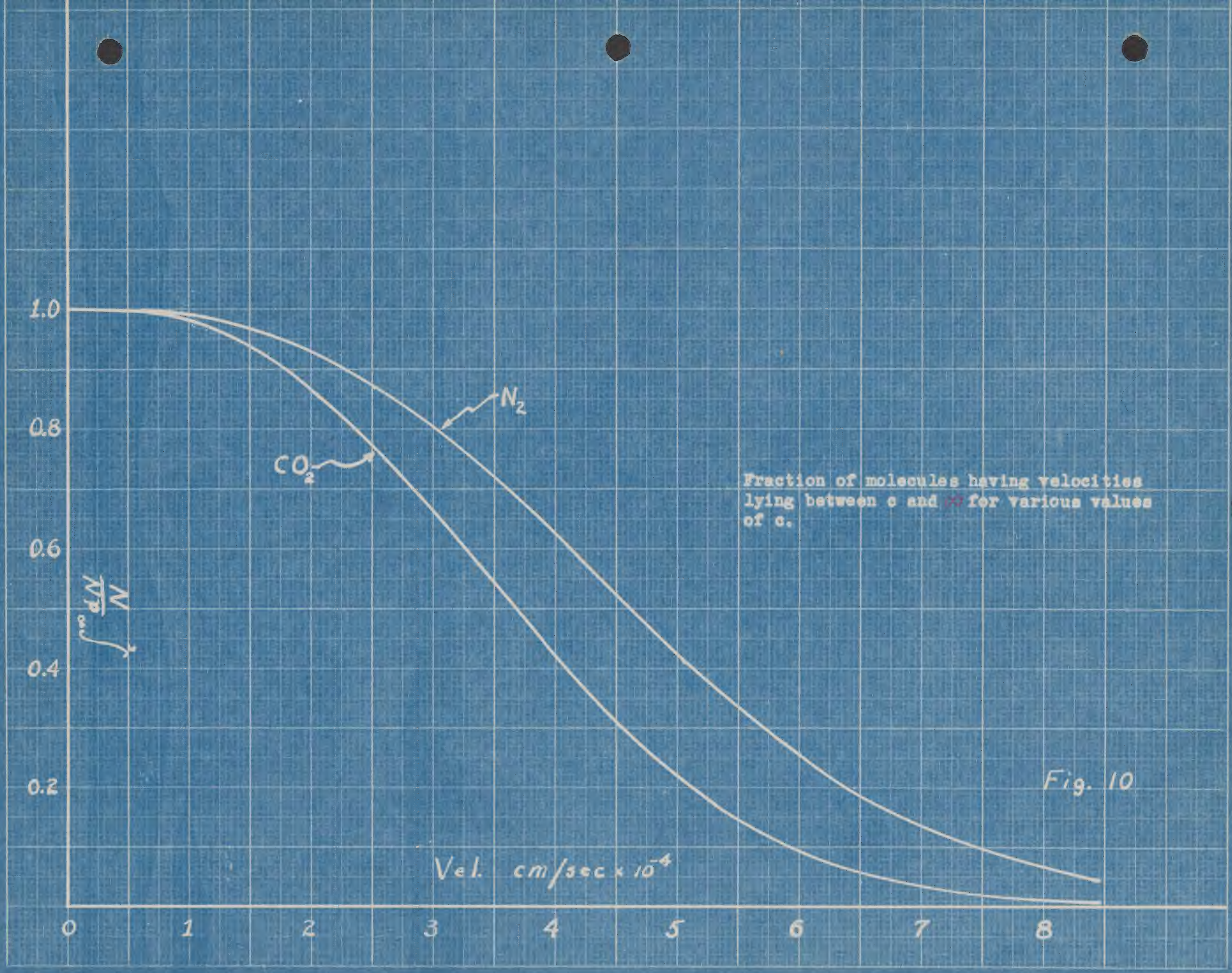
we have $\int \frac{dN}{N} = -\frac{2}{\sqrt{\pi}} x e^{-x^2} + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2}\,dx$

Since the integral $\frac{dN}{N}$ taken from 0 to ∞ is unity, we may write

$$\int_c^\infty \frac{dN}{N} = 1 - \int_0^x \frac{dN}{N} = 1 + \frac{2}{\sqrt{\pi}} xe^{-x^2} - \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2}\,dx$$

Fig. 10 shows graphically the fraction of molecules having velocities greater than those indicated on the abciesa for both nitrogen and carbon dioxide. ($T = 300^\circ$ A) This is the same as the fraction of the molecules entering the periphal openings of the rotor for a given periphal speed.

It is clear from the curve that the fraction of Ng molecules entering the rotor at a given speed of the rotor will be larger than for CO_2. It is also readily observed that the fractional difference of CO_2 and N_2 (difference in ordinates for a given velocity) changes with velocity and reaches a maximum at about 4.5×10^4 cm/sec. Fig. 11 shows this change in fractional difference with velocity, the ordinates being this difference. Values are taken from curves in Fig. 10.



Fraction of molecules having velocities lying between c and ∞ for various values of c.

Fig. 10

Difference in fraction of molecules having velocities lying between c and ∞ for Ng and CO_2 in terms of c.

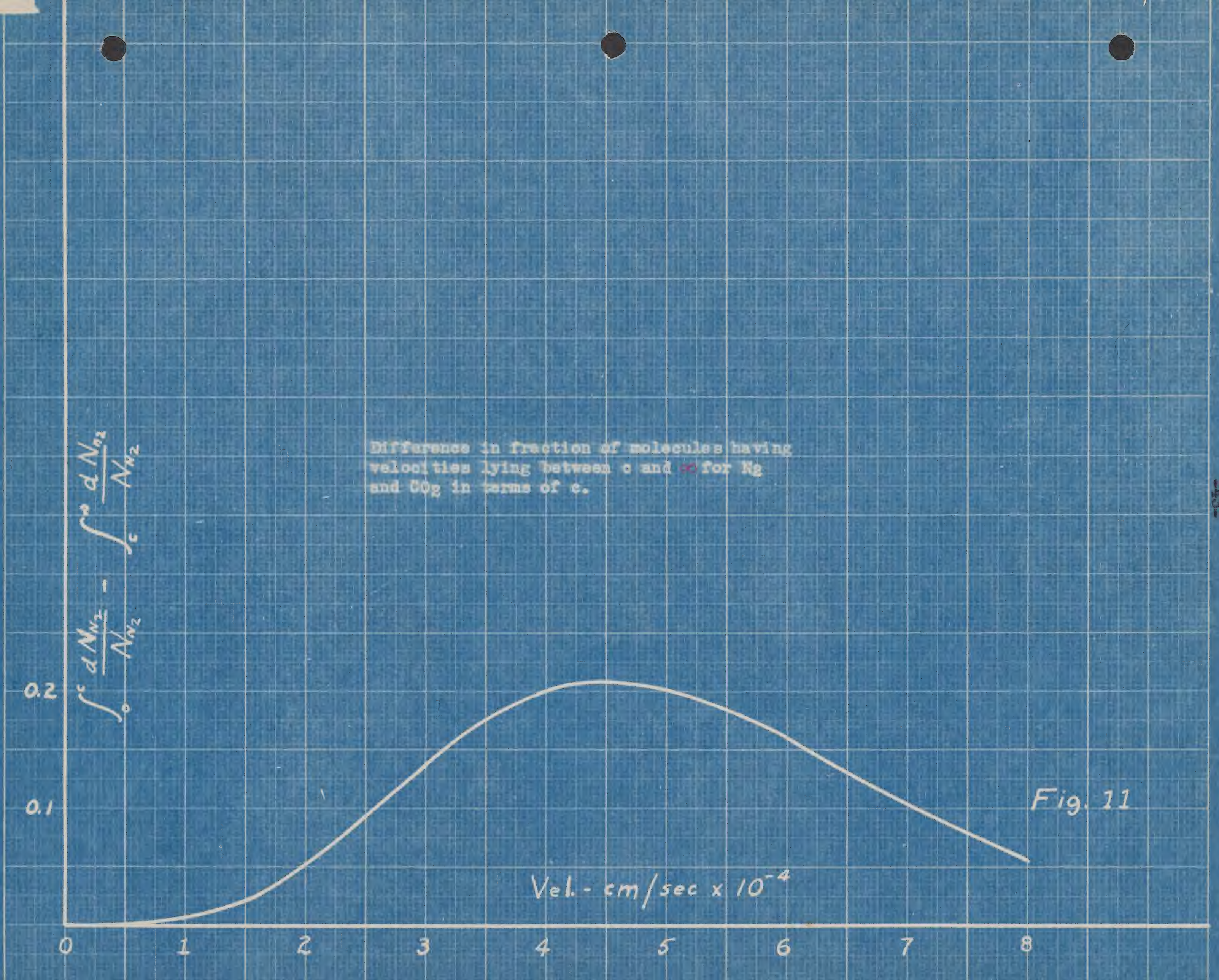


Fig. 11

Maximum Fractional Differences

The maximum fractional difference can be obtained more accurately by equating the first derivative with respect to c, in the equation of the curves in Fig. 11, to 0.

Thus $$0 = \frac{4}{\sqrt{\pi}} \frac{c^2}{\alpha_{N_2}^3} \cdot e^{-\frac{c^2}{\alpha_{N_2}^2}} - \frac{4}{\sqrt{\pi}} \frac{c^2}{\alpha_{CO_2}^3} \cdot e^{-\frac{c^2}{\alpha_{CO_2}^2}}$$

$$\frac{e^{-\frac{c^2}{\alpha_{N_2}^2}}}{\alpha_{N_2}^3} = \frac{e^{-\frac{c^2}{\alpha_{CO_2}^2}}}{\alpha_{CO_2}^3}$$

$$\left(\frac{CO_2}{\alpha_{N_2}}\right)^3 \cdot e^{-\frac{c^2}{\alpha^2 CO_2}} = e^{-\frac{c^2}{\alpha^2 N_2}}$$

From the above values of α_{CO_2} and α_{N_2}, $\frac{\alpha_{CO_2}}{\alpha_{N_2}} = 0.800$

$$(0.8)^3 \cdot e^{\frac{c^2}{\alpha^2 CO_2}} = e^{\frac{c^2}{\alpha^2 N_2}}$$

Since $\log_{10} x = 0.4343 \log_e x$

$$2.303 \log_{10} (0.8)^3 = c^2 \left(\frac{1}{\alpha^2 N_2} - \frac{1}{\alpha^2 CO_2} \right)$$

$$c^2 = 21.3 \times 10^8$$

$$c = 4.61 \times 10^4 \text{ cm/sec}$$

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Separation Factor

While the fractional difference is of interest a more important quantity from the standpoint of separation is the ratio of the fractions of the molecules of the gases for a given speed. This ratio is the separation factor.

For, this ratio is (for N_2 giving the separation factor for N_2)

$$\frac{\int_c^\infty \frac{dN_{N_2}}{N_{N_2}}}{\int_c^\infty \frac{dN_{CO_2}}{N_{CO_2}}} = \frac{\frac{N_2'}{N_2}}{\frac{CO_2'}{CO_2}}$$

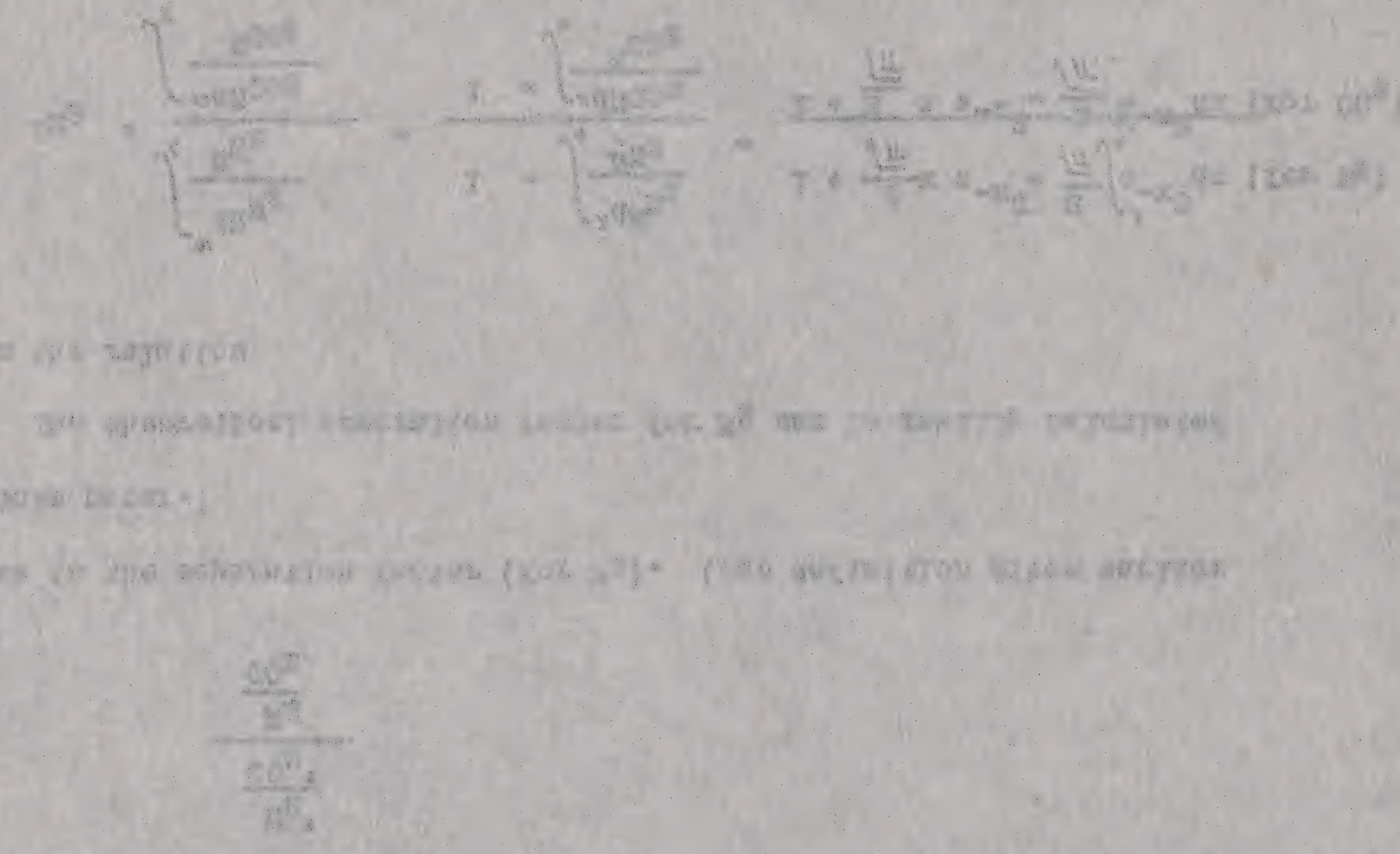
where the prime terms refer to the respective fractions of N_2 and CO_2 entering the rotor and the unprimed terms refer to the respective fractions in the initial mixture. This ratio may then be written

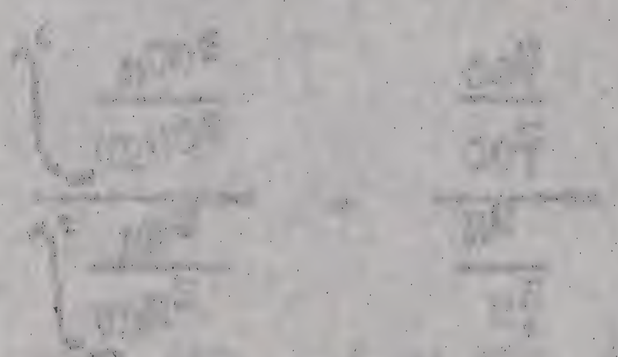
$$\frac{\frac{N_2'}{CO_2'}}{\frac{N_2}{CO_2}}$$

which is the separation factor (for N_2). (See definition given earlier in this paper.)

The theoretical separation factor for N_2 can be readily calculated from the relation

$$S_{N_2} = \frac{\int_c^\infty \frac{dN_{N_2}}{N_{N_2}}}{\int_c^\infty \frac{dN_{CO_2}}{N_{CO_2}}} = \frac{1 - \int_o^\lambda \frac{dN_{N_2}}{N_{N_2}}}{1 - \int_o^\chi \frac{dN_{CO_2}}{N_{CO_2}}} = \frac{1 + \frac{2}{\sqrt{\pi}} x\, e^{-x^2} - \frac{2}{\sqrt{\pi}} \int_o^\lambda e^{-x^2} dx \text{ (for } N_2)}{1 + \frac{2}{\sqrt{\pi}} x\, e^{-x^2} - \frac{2}{\sqrt{\pi}} \int_o^\chi e^{-x^2} dx \text{ (for } CO_2)}$$





Or, the values for the numerator and denominator of this equation can be taken directly from the curves in Fig. 10.

The values of SN_2 for various values of velocity (of rotor periphery) are shown graphically in Fig. 12. It is to be noted that this separation factor curve is similar to the separation factor curve obtained for centrifuge action.

Separation factor S_{N_2} for velocity selection.

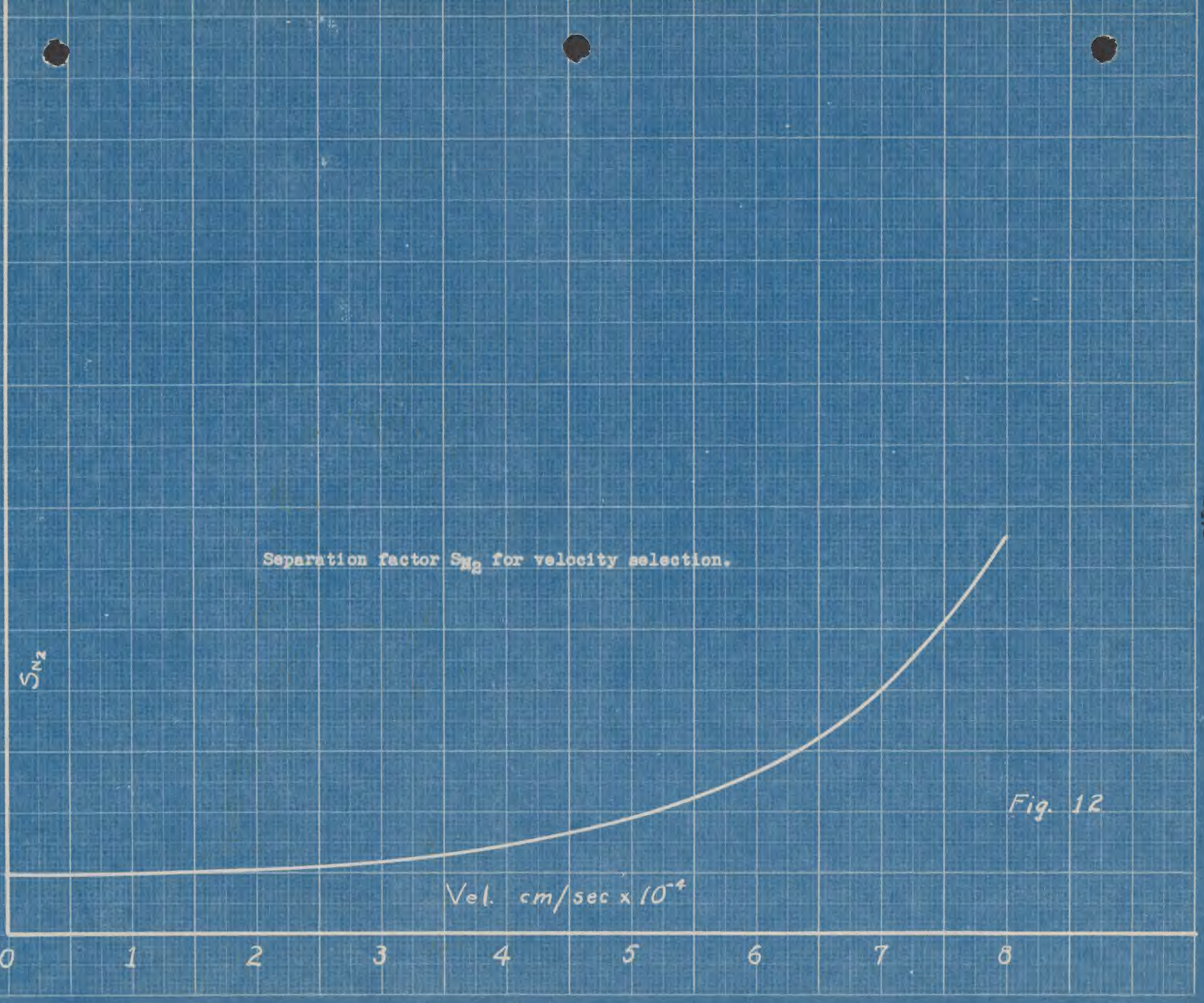


Fig. 12

Effect of Velocity Assumption on Value of S_{N_2}

In the earlier part of this discussion it was assumed that for a given peripheral speed of the rotor, all of the molecules having a speed greater than this particular value will enter the rotor. Obviously, this is not quite true. Rather, all molecules having a velocity component in the direction of motion of the opening greater than the speed of the opening will enter the rotor.

Thus

fraction of molecules of N_2 entering rotor = fraction of molecules of N_2 having velocities lying between c and x

$$\frac{\text{av. vel. compon. of c in direction of motion of opening.}}{c}$$

The average velocity component of c in direction of motion opening is simply

$$(\text{say}) \quad b = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} c \frac{\cos\theta \, d\theta}{\pi}$$

where θ is the angle between c and b.

$$\text{or} \qquad b = \left[c \frac{\sin\theta}{\pi} \right]_{-\frac{\pi}{2}}^{\frac{\pi}{2}} = \frac{2c}{\pi} = 0.637\ c$$

$$\text{Then} \qquad \text{fraction of molecules of } N_2 \text{ entering rotor} = \int_{c}^{\infty} \frac{dN_{N_2}}{N_{N_2}} \times 0.637$$

By similar reasoning to the case of CO_2 results in

$$\text{fraction of molecules of } CO_2 \text{ entering rotor} = \int_{c}^{\infty} \frac{dN_{CO_2}}{N_{CO_2}} \times 0.637$$

Now, the separation factor

$$S_{N_2} = \frac{\text{fraction molecules } N_2 \text{ entering rotor}}{\text{fraction molecules } CO_2 \text{ entering rotor}} \quad \text{(See page)}$$

$$= \frac{\int_c^\infty \frac{dN_{N_2}}{N_2} \times 0.637}{\int_c^\infty \frac{dN_{CO_2}}{N_{CO_2}} \times 0.637} = \frac{\int_c^\infty \frac{dN_{N_2}}{N_2}}{\int_c^\infty \frac{dN_{CO_2}}{N_{CO_2}}}$$

Thus the value of the separation factor is the same as if all molecules having a speed greater than that of the opening, entered the opening.

Effect of Stirring of Gas by Rotor

It has been assumed in all of this section on Velocity Selection that there is a Maximillian distribution of velocity. This cannot be exactly true since the motion of the rotor will undoubtedly disturb this distribution. Thus, experimental results could not be expected to confirm too closely the theoretical computations.

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Total Separation Factor

Since separation by centrifuge action occurs simultaneously with separation by velocity selection the total separation obtained with the triangular rotor will be proportional to each. Thus, the total separation factor will be the product of the separation factor for centrifuge action and the separation factor for velocity selection.

$$\text{Or} \qquad S^{T}_{N_2} = S^{C}_{N_2} \times S^{V}_{N_2}$$

The values of the total separation factor for various speeds is shown in Fig. 13. It is to be noted that the total separation factor $S^{T}_{N_2}$ rises rapidly for the higher peripheral velocities.

CONTENT
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Total separation factor $S^T_{N_2}$ (theoretical).

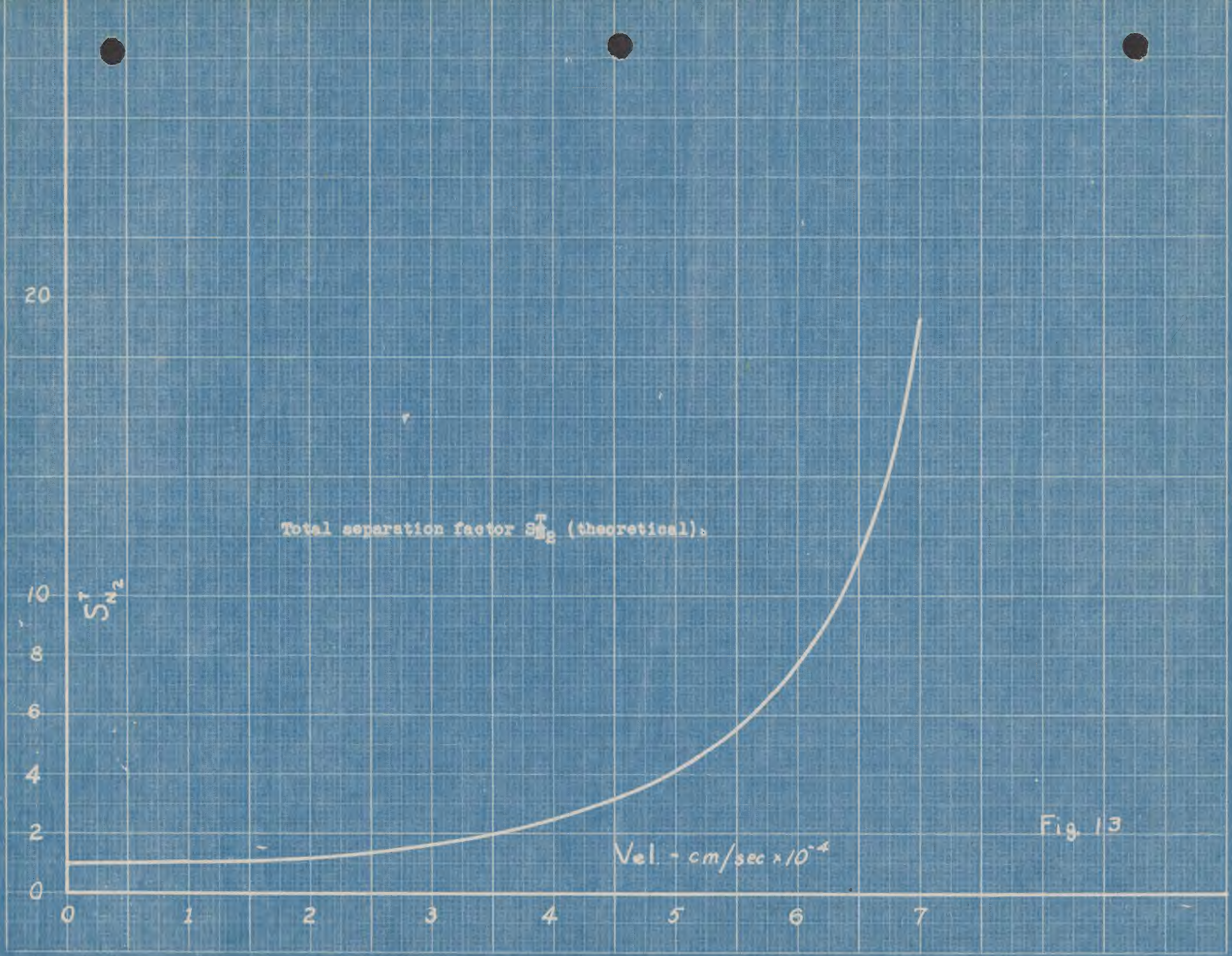

Fig. 13

EXPERIMENT

Apparatus

The apparatus used in checking the theory of separation of two gases of different molecular weight by the principle of velocity selection was practically identical in all respects to the apparatus used in testing the theory of separation by centrifuge action with the exception of the rotor, and a slight difference in mechanical design in that the gas from the rotor was drawn off from a tube extending from the bottom of the rotor through a lower bearing. This apparatus is described in detail earlier in this paper. Nitrogen and carbon dioxide were the gases used.

A horizontal section of the triangular rotor is shown in Fig. 8. A vertical section is similar in form to the round rotor as shown in Fig. 6.

A single piece of Dow metal was used to construct the rotor. The diameter of the rotor was about 4 inches and the diameter of the holes about 1/32 inch.

Procedure

The procedure used in this test was likewise identical in all respects to the procedure used in determining experimentally the separation factor for centrifuge action. The same gases, nitrogen and carbon dioxide, were used.

Observations and Results

The observations made and the results obtained on the separation of nitrogen and carbon dioxide by use of the triangular rotor are given below.

The horizontal rows go in pairs, the first giving the readings for pressure and volume before absorption of the carbon dioxide (P_1 and V_1) and the second row giving the readings for pressure and volume after the gas is passed into and back out of the absorption tube (P_2 and V_2). The horizontal lines in the table indicate a change in the initial gas mixture.

For meaning of symbols used, refer to glossary given earlier in this paper.

For method used in determining S_{N_2} see method used in the determination of the separation factor for separation by centrifuge action.

Results

A graphical representation of the results obtained is given in Fig. 14. The crosses represent the experimental values. The theoretical values of $S^T_{N_2}$ are represented by the curve for purposes of comparison. This curve is the same as Fig. 12.

It is seen that the experimental values lie fairly close to the theoretical values.

Total separation factor $S^{T}_{N_2}$. Curve is theoretical and crosses experimental.

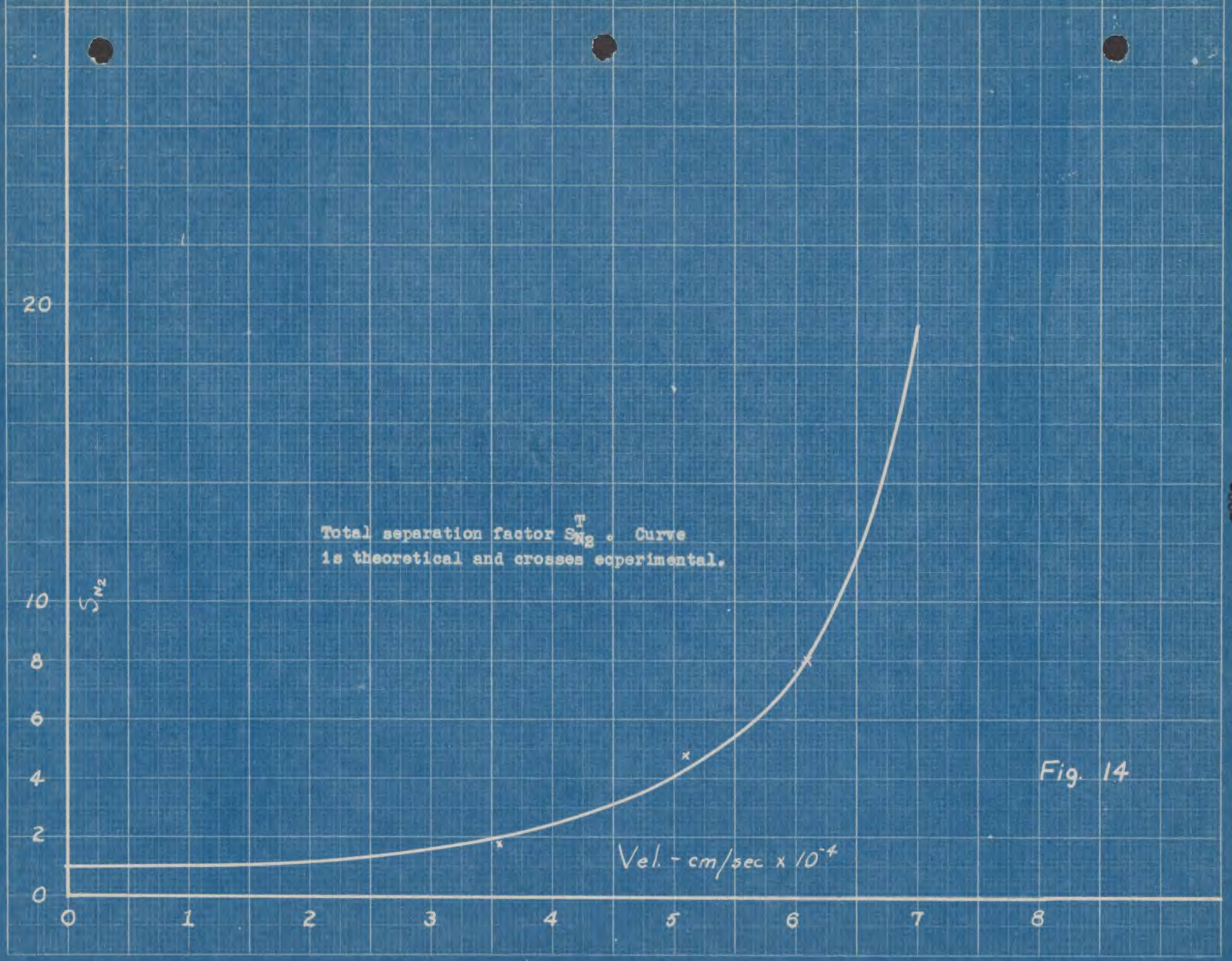

Fig. 14

D = 2r	N	v	L = V	R	$R_{corr.}$	B	P	F	$S^T_{H_2}$
cm	rw/sec	cm/sec	cm	cm	cm	cm Hg	cm Hg		
9.84	0	0	9.8	88.7	58.7	75.02	26.1		
			8.6	95.2	65.2		18.4	62	
	0		17.5	73.4	43.4		49.1		
			13.5	82.1	52.1		36.4	57	
	0	0	10.6	78.9	48.9		36.7		
			10.1	92.5	62.5		22.6	59	
	1150	3.55×10^4	7.6	98.3	68.3		14.3		
			5.9	97.7	67.7		13.2	72	1.8
9.84	0	0	16.1	80.4	50.4	74.65	40.4		
			9.8	78.5	48.5		36.0	54	
	0	0	16.0	76.5	46.5		44.2		
			9.6	74.8	44.8		39.5	54	
	1650	5.09	4.2	99.4	69.4		9.5		
			3.9	99.8	69.8		8.8	86	
	1650	5.09	6.5	98.0	68.0		13.2		
			6.1	98.9	68.9		11.9	85	
	1650	5.09	5.9	98.7	68.7		11.9		
			5.2	98.7	68.7		11.2	83	
								Av. 85	4.84
9.84	0	0	11.8	82.1	52.1	75.34	35.0		
			7.8	81.5	51.5		31.8	60	
	0	0	13.0	81.1	51.1		37.2		
			8.6	81.1	51.1		32.8	58	
	0	0	13.8	81.5	51.5		37.8		
			9.2	81.1	51.1		33.4	59	
	1980	6.12 10	4.9	97.0	67.0		13.2		
			4.2	96.0	66.0		13.5	88	
	1980	6.12	4.4	96.0	66.0		13.7		
			4.4	97.1	67.1		12.6	92	
	1980	6.12	5.6	95.0	65.0		15.9		
			5.6	95.7	65.7		15.2	96	
								Av. 92	8.0

The Separation of the Isotopes of CCl_4 by Centrifuging

Theory

In the case of the mixture of two gases of different atomic weights, either isotopes or not, the separation obtained by the centrifuging process may be expressed as a separation factor which has been demonstrated to be

$$S_A = e^{\frac{(M_B - M_A)\, v^2}{2RT}}$$

where S_A is the separation factor for gas A. When more than two gases or two isotopic constituents of one gas are present it is still possible to think of the separation factor of one constituent with reference to another, or perhaps with reference to some "average" constituent. However, a better picture of the separation process as a whole can be obtained by considering the change in density of the mixture. It is also readily possible to compare the experimental results with the theoretical values from the density change.

Carbon tetrachloride, CCl_4, has four atoms of chlorine and one of carbon. Since carbon has only 0.7% of C^{13} and the rest C^{12}, the isotope C^{13} will be neglected. Chlorine has two isotopes Cl^{35} and Cl^{37} in the abundance ratio of 76 to 24.* CCl_4 can then appear in five different forms $C^{12}Cl_4^{35}$, $C^{12}Cl_3^{35}Cl^{37}$, $C^{12}Cl_2^{35}Cl_2^{37}$, $C^{12}Cl^{35}Cl_3^{37}$ and $C^{12}Cl_4^{37}$. According to Aston* these constituents appear in normal CCl_4 in the following percentages:

A	CCl_4^{35}	31.64%	152
B	$CCl_3^{35}Cl^{37}$	42.18%	154

* Aston, Isotopes,

$$\frac{}{(p^2 - \chi^2)\, A_{\vec{p}}}$$

C	$CCl_2^{35}Cl_2^{37}$	21.09%	156
D	$CCl^{35}Cl_3^{37}$	4.69%	158
E	CCl_4^{37}	0.40%	160

the first column giving the letters by which the constituents will be referred to and the last column being the molecular weights.

In order to set up an equation for the relative densities before and after separation it is convenient to use a separation factor for each constituent referred to some one of the constituents. While there appears to be little choice, it so happens that the average molecular weight is almost exactly 154. For this reason it was used as a reference base.

We will assume now that the carbon tetrachloride is in vapor form in order to use it in the gas centrifuge. Using the notation used above of as the density of the vapor at the center of the rotor and the density at the periphery

$$S_A \quad \frac{\frac{{}_A\rho_o}{{}_B\rho_o}}{\frac{{}_A\rho}{{}_B\rho}} = e^{\frac{(M_B - M_A)\, v^2}{2RT}}$$

Where S_A is separation factor of A referred to standard B.

Similarly $S_B = e^{\frac{(M_B - M_B)\, v^2}{2RT}} = 1$

$$S_C = e^{\frac{(M_B - M_C)\, v^2}{2RT}}$$

$$S_D = e^{\frac{(MB - MD)\, v^2}{2RT}}$$

$$S_y = e^{\frac{(M_B - M_E)\, v^2}{2RT}}$$

Referring to an earlier discussion of the relation between separation and per cent of materials present we find

$$\% A' = \frac{S_A \times \% A \times 100}{\% A\,(S_A - 1) + 100}$$

$$\% B' = \% B$$

$$\% C' = \frac{S_C \times \% C \times 100}{\% C\,(S_C - 1) + 100}$$

$$\% D' = \frac{S_D \times \% D \times 100}{\% D\,(S_D - 1) + 100}$$

$$\% E' = \frac{S_E \times \% E \times 100}{\% E\,(S_E - 1) + 100}$$

where the primes refer to the material after the separation process. The density of the mixture before separation is

$${}_m\rho = \frac{\% A \times {}_A\rho + \% B \times {}_B\rho + \% C \times {}_C\rho + \% D \times {}_D\rho + \% E \times {}_E\rho}{100}$$

and the density of the mixture after separation (at the center the rotor) is

$${}_m\rho_o' = \frac{\% A' \times {}_A\rho_o + \% B' \times {}_B\rho_o + \% C' \times {}_C\rho_o + \% D' \times {}_D\rho_o + \% E' \times {}_E\rho_o}{100}$$

Now since ${}_A\rho = \text{constant} \times \text{molecular weight},^*$ $A = CM_A$, etc. and

${}_A\rho_o = C_o M_A$, etc. the ratio of the densities is

$$\frac{{}_m\rho_o}{{}_m\rho} = \frac{C_o\,(\% A' \times M_A + \% B' \times M_B + \% C' \times M_C + \% D' \times M_D + \% E' \times M_E)}{C\,(\% A \times M_A + \% B \times M_B + \% C \times M_C + \% D \times M_D + \% E \times M_E)}$$

* $PV = RT$; $\rho = \frac{M}{V}$, $P\frac{M}{\rho} = RT$, or $\rho = \frac{R}{RT} M = CM$

While the pressure is less at the center of the rotor for actual operating conditions, the samples are reduced to the same pressure and temperature for purposes of comparison, and for this condition $C = C_o$. The same argument applies if the material is a vapor and is reduced to a liquid for the purpose of comparing densities, since the molecular and mass concentrations will be the same in the liquid as in the vapor state.

Then the density ratio

$$\frac{m\rho_o}{m\rho} = \frac{S_A \times \% A \times 100}{\% A (S_A - 1) + 100} \times M_A + \frac{S_B \times \% B \times 100}{\% B (S_B - 1) + 100} \times M_B$$

$$+ \frac{S_C \times \% C \times 100}{\% C (S_C - 1) + 100} \times M_C + \frac{S_D \times \% D \times 100}{\% D (S_D - 1) + 100} \times M_D$$

$$+ \frac{S_E \times \% E \times 100}{\% E (S_E - 1) + 100} \times M_E$$

$$\frac{\% A \times M_A + \% B \times M_B + \% C \times M_C + \% D \times M_D + \% E \times M_E}{}$$

$$= \frac{e^{\frac{(M_B - M_A)}{2RT} v^2} \times \% A \times 100 \times M_A}{\% A \left(e^{\frac{(M_B - M_A)}{2RT} v^2} - 1\right) + 100}$$

$$+ \% B \times M_B + \frac{e^{\frac{(M_B - M_C)}{2RT} v^2} \times \% C \times 100 \times M_B}{\% C \left(e^{\frac{(M_B - M_C)}{2RT} v^2} - 1\right) + 100}$$

$$+ \frac{e^{\frac{(M_B - M_D)}{2RT} v^2} \times \% D \times 100 \times M_D}{\% D \left(e^{\frac{(M_B - M_D)}{2RT} v^2} - 1\right) + 100}$$

$$\frac{\% A \times M_A + \% B \times M_B e^{\frac{(M_B - M_E)v^2}{2RT}} + \% C \times M_C e^{\frac{(M_C - M_E)v^2}{2RT}} + \% D \times M_D e^{\frac{(M_D - M_E)v^2}{2RT}} + \% E \times M_E}{\% A \times M_A + \% B \times M_B + \% C \times M_C + \% D \times M_D + \% E \times M_E}$$

$$= \frac{\% A \times 100 \times M_A e^{-\frac{v^2}{RT}}}{\% A (e^{\frac{v^2}{RT}} - 1) + 100} + \frac{B \times M_B}{} + \frac{\% C \times 100 \times M_C e^{-\frac{v^2}{RT}}}{\% C (e^{-\frac{v^2}{RT}} - 1) + 100}$$

$$+ \frac{\% D \times 100 \times M_D e^{-\frac{2v^2}{RT}}}{\% D (e^{-\frac{2v^2}{RT}} - 1) + 100} + \frac{\% E \times 100 \times M_E e^{-\frac{3v^2}{RT}}}{\% E (e^{-\frac{3v^2}{RT}} - 1) + 100}$$

$$\frac{}{\% A \times M_A + \% B \times M_B + \% C \times M_C + \% D \times M_D + \% E \times M_E}$$

This gives the density ratio as a function of the peripheral velocity and is a fraction less than one as it stands. The reciprocal could obviously be used if desired.

This equation would presumably hold for the case of the hollow rotor described below (Fig. 15) as the process of separation is essentially the same for the early stages of evaporation. In this case the CCl_4 in liquid form is at the periphery of the cavity and as it evaporates the lighter material will pass towards the center of rotor while some of the heavier constituents will return to the liquid.

EXPERIMENT

Apparatus

The round rotor used in the separation of N_2 and CO_2 and shown in Fig. 6 was first utilized in an attempt to separate the isotopes of CCl_4. A schematic diagram of the auxiliary apparatus is shown in Fig. 15. The flask F, partly filled with CCl_4, was connected in the system only when the round rotor was used as explained below. The traps were immersed in a mixture of solid CO_2 and alcohol in order to catch the CCl_4 as it passed out of the centrifuge C.

The four traps grouped together were connected by heavy rubber tubing and provided with pinch clamps P so that various parts of the "run" could be caught separately.

Later runs were made with a hollow rotor (round) a vertical section of which is shown in Fig. 16. Liquid CCl_4 was placed inside this rotor, it having no holes in its periphery. T is the supporting tube.

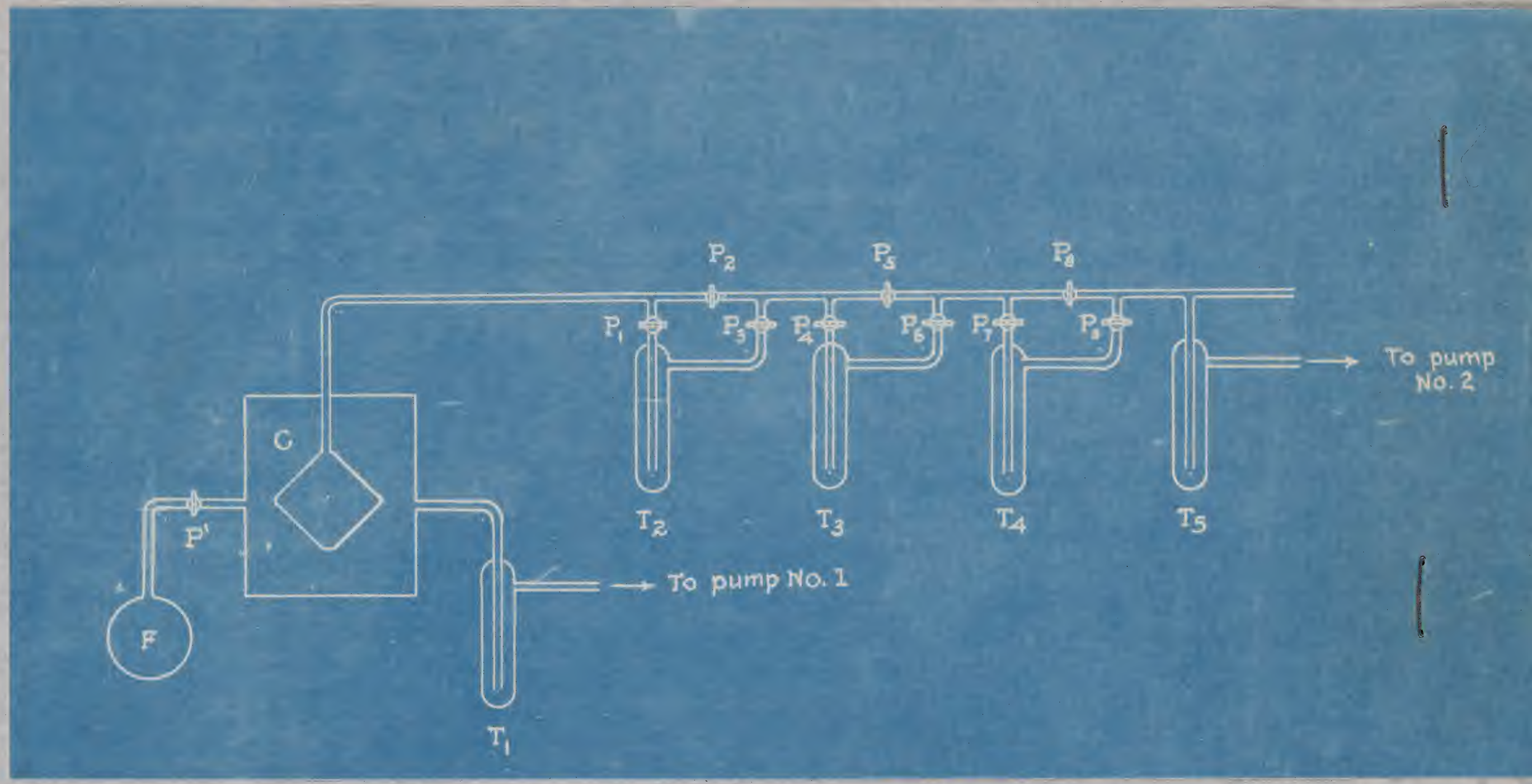

Figure 15

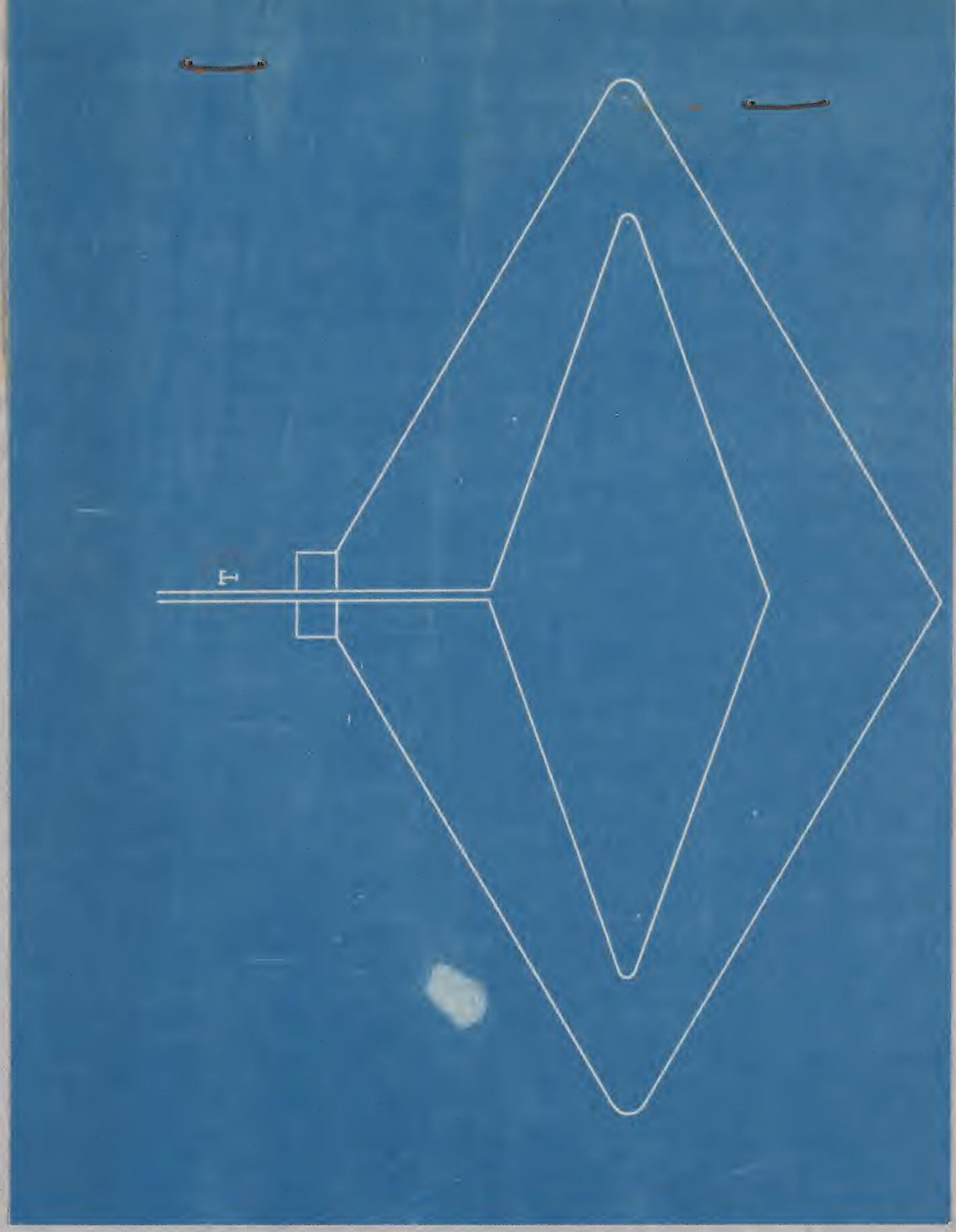

Figure 16

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Procedure

The separation of the isotopes of CCl_4 was first tried with the round rotor as mentioned above. A sample of C.P. (Baker's) CCl_4 was placed in the flask F (Fig. 15) and frozen with the aid of solid carbon dioxide. The dry ice was kept around the flask while P^1 was opened and the pumps started. The air was completely removed from the system before the flask was allowed to warm up.

With a dry-ice-alcohol mixture around each trap the centrifuge was brought up to a speed of 1500 r.p.s. CCl_4 distilled over from F into the centrifuge chamber, a large part condensing and freezing again in trap T_1. A lighter sample passed through the centrifuge and was caught in trap T_2.

After a one-hour run only one drop of the lighter sample was found collected in T_2. While undoubtedly this sample contained a predominance of the lighter isotopes of CCl_4, there was not a sufficient quantity to determine its density by the means available.

In order to increase the rate of separation a hollow rotor was made from duralumin, a section of which is shown in Fig. 16. A sample of about 30 cm^3 of CCl_4 was placed inside this rotor and cooled with dry ice. The centrifuge was quickly reassembled, P^1 closed the pumps started and the rotor set in motion. Pinch clamps P_1 and P_2 were tightly closed.

When the rotor reached a speed of 1500 r.p.s. the pinch clamps were manipulated so that the first part of the run was caught in T_2. later parts of the run were caught in the remaining traps.

All samples were carefully distilled in order to get rid of impurities.

The density of the sample of CCl_4 caught in T was compared with the density of the initial sample by means of a sensitive hydrometer. The hydrometer itself consisted of a globule of glass having a volume of about 1 cm^3 and it was weighted with small bits of copper wire until it would barely float in the lighter sample. The stem of the hydrometer consisted of 2 cm length of tungstem wire fastened at its lower end to the glass float. The diameter of the wire was 0.005 inch.

Since temperature affects the density of the CCl_4, the standard sample and the light sample were placed in test tubes side by side and both covered with the same glass vessel lined with copper. The whole was placed in a basement room of constant temperature and allowed to stand for four or five hours. A comparison of densities at that time showed a difference in the two samples, the standard being the heavier of the two.

Observations and Results

Hollow rotor

Outside diameter 9.9 cm

Inside diameter 8.6 cm

Speed of rotor - 1500 r.p.s.

Time of run for 1st light sample - 6 minutes

Time of run for 2nd light sample - 9 minutes

Time of run for 3rd light sample - 13 minutes

No CCl_4 left in rotor at end of run

Hydrometer test with standard against 1st sample gave a difference in the depth of hydrometer of 1.5 cm. This represents a change in volume of displacement of

$$\Delta V = \pi r^2 h = 3.14\ (0.0025 \times 2.54)^2 \times 1.5 = 0.00019\ cm^3$$

Relative density

$$\frac{D_1}{D_2} = \frac{V_2}{V_1} \qquad \frac{V_1 + \Delta V}{V_1} = 1.00019$$

or, expressing it the other way, the relative density is

$$\frac{D_2}{D_1} = 0.99981$$

or a change in density of about two parts in ten thousand.

If appropriate values are substituted in the equation for the relative density derived above, we find the value to be 0.9966 using the maximum inside diamter of the rotor. This value for the diameter is obviously too large. However, due to the shape of the interior of the rotor and the contimuously changing volume of the liquid due to evaporation, it is rather difficult to even estimate the correct diameter to use. Since the diameter appears squared in the exponent of epsilon,

thus greatly magnifying any change in its value in the theoretical value of relative density, it may at least be said that the experimental results are not in disagreement with theory.

Unless impurities were present in the original sample which were not removed by redistillation, the first-run sample must undoubtedly contain a predominance of the lighter isotopes of chlorine.

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ACKNOWLEDGMENTS

I wish to express my deep appreciation to Dr. J. W. Beams, who suggested this problem, for his able suggestions, his wholehearted interest and helpful encouragement during the time this research was in progress. I am also indebted to others in the Department of Physics and in particular to Mr. Linke who constructed the centrifuge itself, assisted in its repair, and made many helpful suggestions.

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